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The Journal *of the* SOCIETY OF DYERS AND COLOURISTS

Volume 69 Number 8

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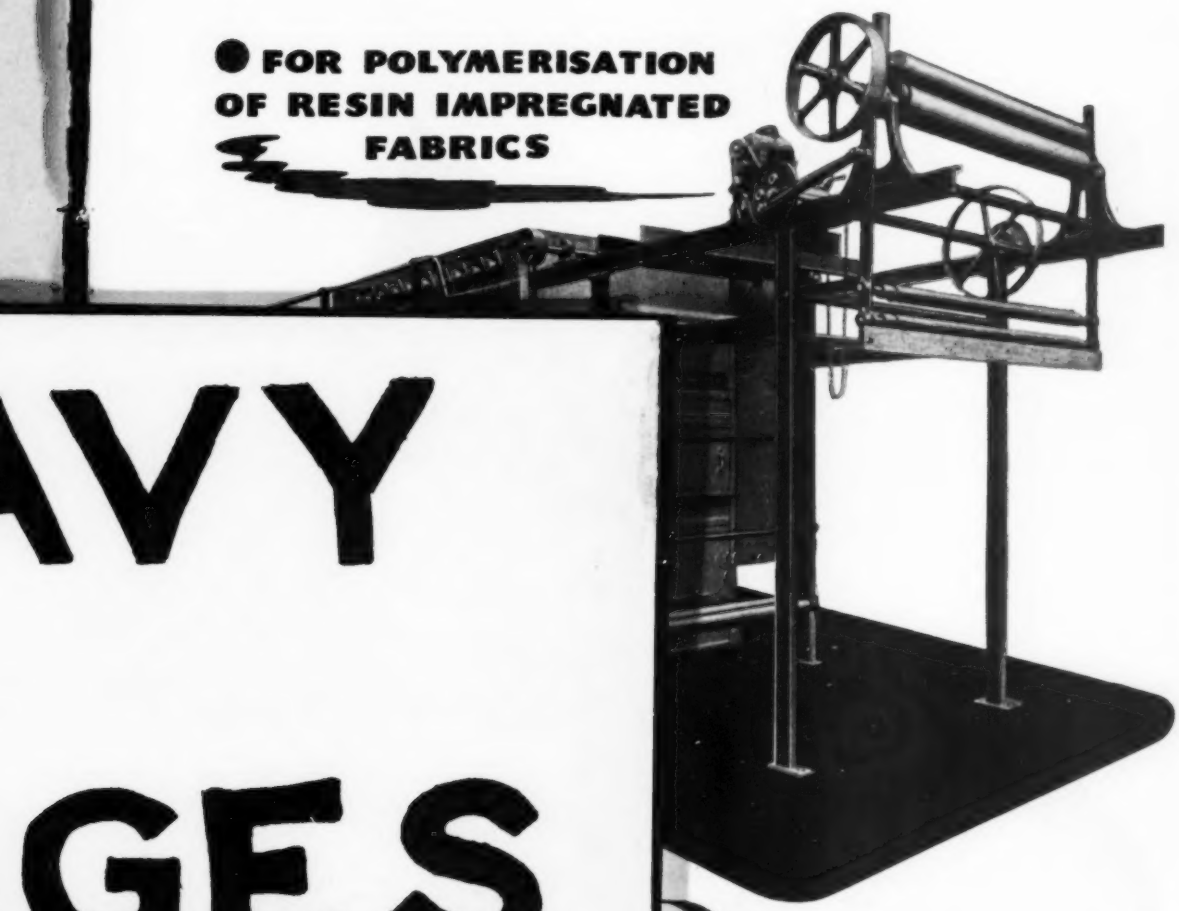

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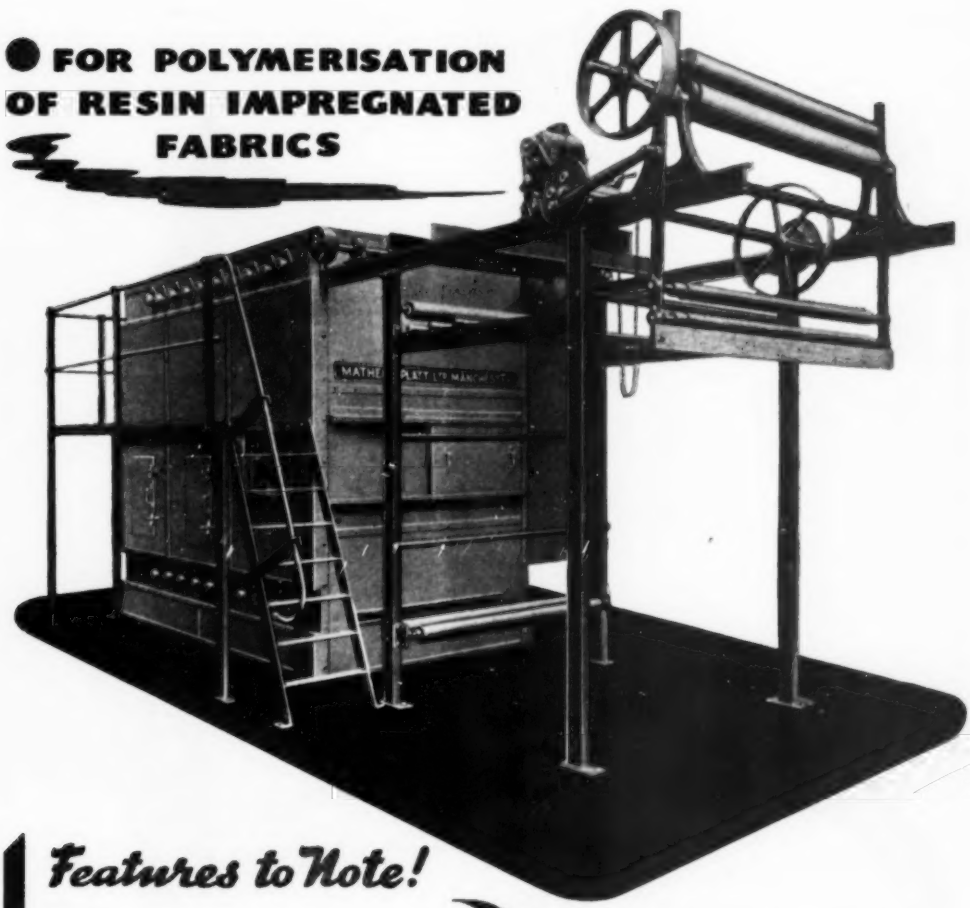

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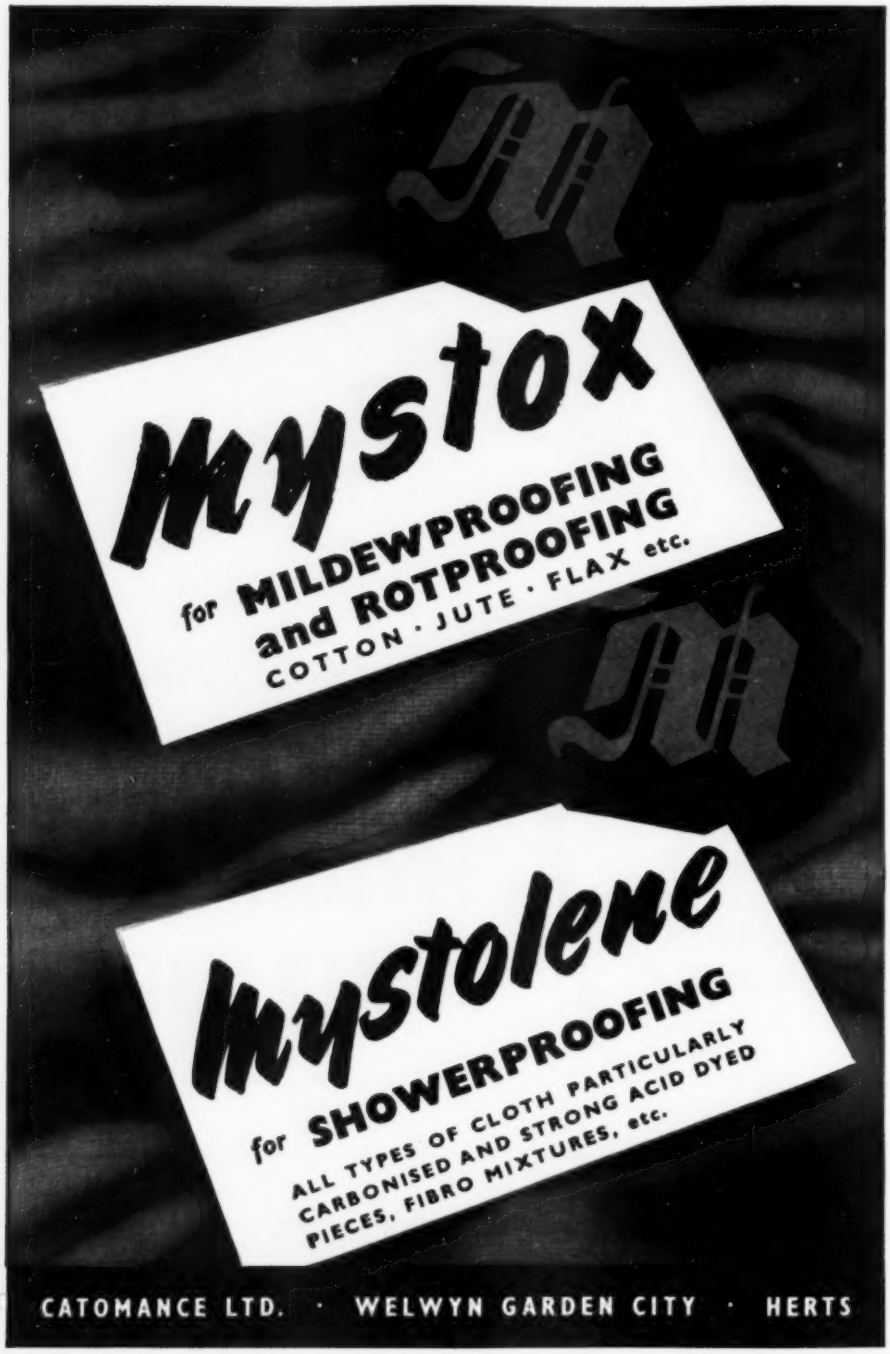
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All Meetings in St. Enoch Hotel, Glasgow, at 7.0 p.m., unless otherwise stated

1953

Tuesday 29th Sept. — Dr. I. S. M. Walls (I.C.I.). *The Dyeing and Finishing of Fabrics containing the Newer Synthetic Fibres*

Tuesday 27th Oct. — Dr. G. H. Lister (Sandoz Products Ltd.). *The Migration Properties of Acid and Chrome Dyestuffs*

Tuesday 17th Nov. — J. S. Ingham, Esq., M.Sc., F.R.I.C. (Marks and Spencer Ltd.). *Problems of Colour Fastness and Finish*

Thursday 10th Dec. — Dr. J. F. Gaunt (Messrs. Patons & Baldwins Ltd.), Scottish Woollen Technical College, Galashiels. *A discussion on the Relative Merits of Different Methods of Applying Chrome Dyes*

Tuesday 15th Dec. — Prof. P. D. Ritchie. *Links between the Textile and Plastics Industries*

MIDLANDS SECTION

Except when stated otherwise, Lecture Meetings commence at 7.0 p.m.

1953

Wednesday 30th Sept. — C. O. Clark, Esq., F.T.I. *Some Authentic Records of the Craft of Dyeing.* College of Technology, Leicester

Thursday 22nd Oct. — S. Burgess, Esq., A.M.C.T. *Economic and Technical Difficulties in meeting Fastness Requirements.* The College, Loughborough

Tuesday 3rd Nov. — D. N. Marvin, Esq., A.R.I.C., A.T.I. (Joint meeting with Hinckley Textile Society). *Some Properties of Terylene.* College of Further Education, Hinckley. 7.15 p.m.

Wednesday 18th Nov. — H. R. Hadfield, Esq., M.Sc. *The Dyeing of Caprolactam Fibres (Perlon etc.).* Midland Hotel, Derby

Saturday 21st Nov. — LADIES EVENING — DINNER DANCE, Black Boy Hotel, Nottingham

Wednesday 2nd Dec. — R. W. Speke, Esq., B.Sc. *A Study of Variables in Padding.* Black Boy Hotel, Nottingham

1954

Wednesday 20th Jan. — J. Payne, Esq., B.Sc. *Silicon Chemicals in Textile Finishing.* College of Technology, Leicester

Wednesday 24th Feb. — Douglas Haigh, Esq., A.T.I. *Some recent researches in the Dyeing of Felt.* Masonic Hall, Nuneaton

Thursday 4th March — R. F. Wilson, Esq. (B.C.C.) (Joint meeting with the Nottingham Textile Society). *Colour.* Gas Theatre, Nottingham

Wednesday 17th March — G. H. Lister, Esq., B.Sc., Ph.D. *The Migration Properties of Acid and Chrome Dyes.* Victoria Station Hotel, Nottingham

Friday 26th March — MIDLANDS SECTION DINNER. King's Head Hotel, Loughborough

MIDLANDS SECTION (*continued*)

Wednesday 7th April — ANNUAL GENERAL MEETING OF SECTION. J. A. Potter, Esq., M.A. *Dyeing and Finishing Synthetic Fibres in the Hosiery Industry.* King's Head Hotel, Loughborough

LONDON SECTION

All Meetings will be held at the Royal Society, Burlington House, Piccadilly, London W.1, at 6.0 p.m. unless otherwise stated

1953

Friday 2nd Oct. — C. R. M. Oehlcke (Newcol Ltd.). *The Use of Organic Pigments in Modern Plastics*

Friday 6th Nov. — Messrs. B. Kramrisch and A. Bratt (Clayton Aniline Co. Ltd.). *Problems of the Garment Dyer and Finisher, including the Dyeing of Buttons*

Thursday 3rd Dec. — Alec B. Hunter (Warner & Sons Ltd.). *Design and Colour*

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Thursday 7th Jan. — Dr. G. T. Douglas (I.C.I. Ltd.). *The Dyeing of Synthetic Fibres*

Friday 5th Feb. — C. P. Tattersfield (Courtaulds Ltd.). *Dyeing and Finishing in relation to Use-Development Work*

Friday 5th March — *The London Lecture.* Subject, Speaker and venue to be given

MANCHESTER SECTION

Unless otherwise stated, meetings take place at the Textile Institute, 10 Blackfriars Street, Manchester 3, and commence at 6.30 p.m

1953

Friday 18th Sept. — T. Green, Esq. (Clayton Aniline Co. Ltd.) *The Near Infra-red Reflectance of Dyed Materials*

Friday 16th Oct. — F. Ward, Esq. (Courtaulds Ltd.). *The Principles and Practice of Flameproofing Textiles*

Friday 20th Nov. — LADIES' EVENING *How do I know what to buy?* Commences at 7.0 p.m. Details will be announced later

Friday 18th Dec. — Details to be announced later

1954

Friday 15th Jan. — S. Blackburn Esq., and M. R. Fox, Esq. (I.C.I. Ltd., Dyestuffs Divn.). *The Behaviour of Leuco Vat Dyes above 100° C.*

WEST RIDING SECTION

Meetings held at the Victoria Hotel, Bradford, at 7.15 p.m. unless otherwise stated

1953

Friday 16th Oct. — SUPPER AND SMOKER

Thursday 29th Oct. — Sir Ernest Goodale, C.B.E., M.C. *Ancient and Modern Textile Production in London and the Home Counties*

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NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–6 of the January 1953 and pages 229–232 of the July 1953 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138–9). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

The Dyeing of Viscose Rayon at High Temperatures *K. Butterworth*

The Textile Trade and the Newer Fibres *F. H. Clayton*

Ancient and Modern Textile Production in London and the Home Counties *Sir Ernest Goodale*

Pressure Dyeing and Bleaching with special reference to Recent Developments *F. H. Marsh*

The Heat Setting of Terylene Polyester Filament Fabrics in relation to Dyeing and Finishing *D. N. Mavin*

Studies in the Printing of Terylene Polyester Fibre *A. G. H. Michie*

Fugitive Tinting with particular reference to Celafibre *H. C. Olpin and A. J. Wesson*

Fuel Efficiency in the Dyeing and Finishing Trades *W. Short*

The Uses of Microscopy in Textile Dyeing and Finishing *G. G. Taylor and J. C. Brown*

COMMUNICATIONS

Polymerisation of a Series of Vinyl Monomers in Wool *N. K. Boardman and M. Lipson*

Studies in the Fundamental Processes of Textile Printing.

VI—The Transfer of Disperse and Water-soluble Dyes to Nylon during Steaming *E. H. Daruwalla and H. A. Turner*

Absorptiometric Colorimetry in the Textile Laboratory *C. H. Giles and J. S. Shaw*

Observations on Some Commercial Colour Matching Lamps *J. C. Guthrie and P. H. Oliver*

Further Observations on the Effects of Evaporating Water from Cotton Cellulose *G. W. Madaras and H. A. Turner*

Some Experiments on the Over-dyeing of Nylon *C. D. O'Briain and R. H. Peters*

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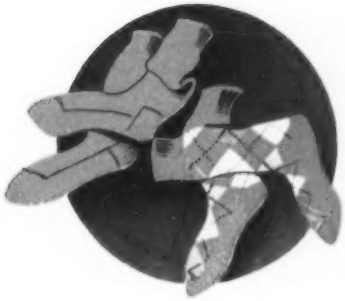

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THE JOURNAL

OF THE

Society of Dyers and Colourists

Volume 69 Number 8 AUGUST 1953 *Issued Monthly*

Proceedings of the Society

THE TENTH JOHN MERCER LECTURE

The Coloration of Leather

J. R. Blockey and D. H. Tuck

Meeting held at the Royal Institution, London W. 1, on 9th April 1953, Mr. H. H. Bowen, President of the Society, in the chair

1. INTRODUCTION

In paying tribute to John Mercer this evening, we thought it might be interesting to compare leather as John Mercer knew it with modern leather. In the nineteenth century, leather was still produced by traditional methods which had been in use for centuries; and very little scientific investigation of leather manufacture took place in this country until the beginning of the Professor Proctor era at Leeds University at the end of the nineteenth century. The leather that Mercer wore on the soles of his boots would be tanned by the vegetable tanning process, using oak bark and other similar materials, and the total time for the complete leather to be produced would have been nearly two years. Today sole leather is produced with the aid of concentrated tanning extracts and strict scientific control of the processing conditions in three to four months. The uppers to Mercer's boots or shoes would have been tanned with vegetable tannins, calf or light hide being used, and after tanning the leather being brush-dyed with natural dyes and impregnated with oils and greases to make it waterproof. Modern shoe upper leather is tanned with chromium salts and is produced more quickly and with a greater variety of colours and finishes than in Mercer's day. Two other tannages used in the nineteenth century employed in one case alum and in the other case oxidisable oils for chamoising. Owing to lack of stability, the alum tawing of skins has been largely abandoned, and has been replaced by white chrome, zirconium, and synthetic-resin tannages. Oil tanning is still widely practised, but the latest modification to oil tanning, calling for the use of oxidation catalysts of the cobalt linoleate type, has greatly speeded up the oil tanning process.

To summarise the changes in tanning techniques, the older, slower methods of both tanning and leather dressing have been replaced by quicker processes in order to produce leather at a competitive price. The main change in leather coloration has been the replacement of naturally occurring dyes by an ever widening range of synthetic dyes, thus giving increasing scope to the leather dyer. During the past twenty years there has also been the development of the surface pigment colouring of leather. The early pigment finishes were developed from the paint industry, but the surface colouring of leather has now become a highly skilled scientific process. The coloration of leather has been further complicated by the introduction of other methods of tanning and by the dictates of changes in fashion. The competition from plastics and synthetic fibres has provided the leather trade with a challenge, to which it is responding by spending much money and thought in seeking a better understanding of leather production, the kind of research which was dear to John Mercer.

2. DEFINITION OF LEATHER

Before discussing the coloration of leather, we should attempt to define leather, a very difficult matter, as we hope to show. Leather can be defined briefly as the end product of tanning, a process which converts a putrescible protein into a stable, non-putrescible substance. The main leather-forming protein in hides and skins is collagen, an amphoteric protein with an isoelectric point of pH 5·3. There are several other proteins in skin, but these are mainly restrictive networks of a structural nature. The empirical composition of collagen can be readily determined, and the constitution is generally assumed to be a chain molecule 640 A. long, consisting of polypeptide chains. These chains lie parallel and non-parallel, giving respectively crystalline and amorphous regions to the fibrils into which they are built. According to Burton and Reed [1] the fibril is of uniform thickness for any particular skin; for example, cowhide collagen has fibrils 1100 A. in diameter and could contain 19,000 molecular chains. Projecting from the polypeptide backbone are various ionisable

amino acid residues and in aqueous phase these side-chains exist as zwitterions, formed by positively charged amino side groups and negatively charged carboxyl side groups.

The unit fibrils are built up into larger units and fibres, and these in turn are held in fibre bundles by restrictive networks, the fibre bundles being interwoven into the general skin structure.

During the preparation of the hide or skin for tanning, the fibres are treated with alkalis such as lime and caustic soda, alkaline reducing agents such as sodium sulphide for unhairing, and pancreatic enzymes. All these materials, together with various neutral salts such as calcium chloride, have a hydrolytic effect on the collagen, and according to the pH, time, temperature, and degree of agitation, the protein is modified by hydrolysis of the side-chains and the weakening of cohesive forces in the fibre structure. The extent of this change is indicated by the shrinkage temperature of the pelt, which falls progressively during hydrolytic processes. Over several days the shrinkage temperature can fall as much as 5°C., but during tanning it rises. The general stability of any leather is indicated by its thermal stability. The important point we wish to make here is that the chemical reactivity of collagen with ions of all kinds is modified during the pretanning processes.

The stabilisation of the protein by tanning can be carried out in many ways, the earliest method, which is still widely used, being with the aid of the natural or vegetable tannins. The natural tannins have still to be isolated in their pure forms, and little is known about their chemical composition. The mechanism of combination with collagen is still not known with certainty, but the latest theory postulates that the combination between vegetable tannins and collagen is by hydrogen bonding along the backbone of the collagen molecules. Vegetable-tanned leather generally reacts as if it carried a weak negative charge, inasmuch as it has poor affinity for anions. According to Otto [2] the reactivity of untanned collagen and of vegetable-tanned leather with anionic dyes is the same, so that vegetable tanning does not seem to occur at the amino side-chain groupings. The thermal stability of vegetable-tanned leather does not generally exceed 60°C. Treatment with alkalis results in a reversal of the tannage, and treatment with acid solutions below pH 3·0 can cause weakening of the fibre structure. The point to be emphasised here is that, in the dyeing of vegetable-tanned leathers, there are severe limitations on the pH and the temperature which may be employed with safety. The stability of vegetable-tanned leather to oxidising and reducing agents is also very low, and this, again, limits the range of dyeing techniques.

The tanning of collagen with basic chromic sulphate is generally considered to be due to the formation of complex chrome bridges between adjacent polypeptide chains, the chromium attaching itself initially to the acidic carboxyl side-chains. The tannage is very rapid, and increasing chrome contents give increasing thermal stability. Most commercial chrome leathers can be boiled in water for one to two minutes, but lightly tanned skins such as glove leathers have less stability in hot water. The polarity and the quantity of the chrome complex formed in the tannage are very important, as they determine the nature and the strength of the electric charge carried by the leather.

Tannage with excess of cationic chromium results in a leather with a positive charge, arising from the basic side-chains, and such a leather has high affinity for anions of all kinds. If the chromium is made non-ionic or anionic by the addition of complex-forming salts of weak organic acids, e.g. sodium formate or sodium adipate, then the polarity of the leather changes and the affinity for anions is reduced. This effect is noticeable mainly in the dyeing of suède leather from concentrated dyebaths.

Chrome-tanned leather is stable to weakly alkaline or acidic solutions, and can be processed over the pH range 3·5–9·0 without difficulty. This fact allows a good deal of scope in the dyeing of chrome leather.

The tannage of collagen with formaldehyde occurs in alkaline solutions and results in a combination between the basic side-chains and the formaldehyde. It has been suggested that formaldehyde may also form cross-linkages between adjacent polypeptide chains. The thermal stability of formaldehyde-tanned leather is higher than that of vegetable-tanned leather, but not so high as that of chrome-tanned, lying in the range 70–75°C. The reactivity of formaldehyde-tanned leather with anions is low, and formaldehyde leather is generally mordanted with a chrome salt before being dyed with anionic dyes.

Other methods of tanning include the use of oil, alum, synthetic tannins, zirconium, and synthetic-resin tannages, as well as combination tannages of many kinds. From this it can be seen that there is no single substance called leather, and that each tanner's leather has to be processed on its own merits.

3. HISTOLOGY— SKIN STRUCTURE

Having considered the possible chemical constitution and composition, we must now consider the physical structure of leather and its bearing on coloration processes. Most hides and skins are built up from three distinct layers— the corium major, the corium minor, and the adipose tissue of the flesh-side layer (Fig. 1). The main strength of the hide or skin is in the corium major, an interwoven fibre structure which is close and tightly woven in the case of calf and goat, and less tightly woven in the case of sheep. This is protected on the surface by the corium minor, which is a densely interwoven fibred layer, containing hair or wool follicles, muscles, and glands, and giving to the skin its characteristic grain pattern. The flesh side of the skin consists of loosely packed fibres, fat cells, veins, and tissues, which have to be removed to allow penetration of chemicals into the corium.

The penetration of dyes into leather is mainly from the flesh side, the corium minor being only relatively slowly penetrated owing to its denser fibre structure. When complete penetration is required, it is necessary to use dyes of low molecular weight which have good solubility and controllable rates of dyeing. The fibre structure can act as a

membrane and filter out dyes of differing molecular weight from mixtures, often giving, with dyes of unequal dyeing properties, different colours to the surface and to the dyed cut edge. The surface of the corium minor is more tightly woven down the backbone of the skin, while the edges are more loosely woven and open. Thus, variation in levelness of dyeing from one part of a skin to another part of the same skin can occur, while difference in colour from one skin to another can also happen, often because of differences in the age, sex, breed, and feeding of the animals, even when all skins are processed together.

For the same reason the brightness and fullness of the colour can be changed by variations in the surface density and texture. The presence of grain defects of all kinds on the corium minor—scars, scratches, insect damages, and so on—causes irregularity of dyeing. Some of the grain faults are open and absorbent, while healed scars are practically waterproof owing to the formation of a hard protective film round the infected areas.

All raw skins contain natural greases in varying proportions of, say, 2% in calf up to 25% in some kinds of sheep. The presence of this grease, as either glycerides, fatty acids, or soaps, causes irregular dyeing, and as a general rule very greasy skins are solvent-degreased before or after tanning, but in mineral tanning it is essential to remove as much of the grease as possible before tanning, to prevent the formation of metallic soaps.

4. THEORY OF LEATHER DYEING

A theory of leather dyeing has recently been put forward by Otto [2], in which he states that the combination between dyes and leather is due to weak polar forces, not to salt linkages, as had generally been assumed.

Anionic dyes are attracted to the positively charged amino side-chains of the protein, while cationic dyes are attracted to the negatively charged carboxyl side-chains. The method of preparing the skin for tanning and the method of tanning both vary the polarity of the leather, while the polarity of the dye is determined by its chemical constitution. In acid solutions all leathers take on a net positive charge of varying strength and have affinity for anions. In chrome leather all the amino side-chains are unoccupied with tanning agents, so that chrome leather has high affinity for anions, but poor affinity for cations. At the National Leathersellers' College we recently investigated the action

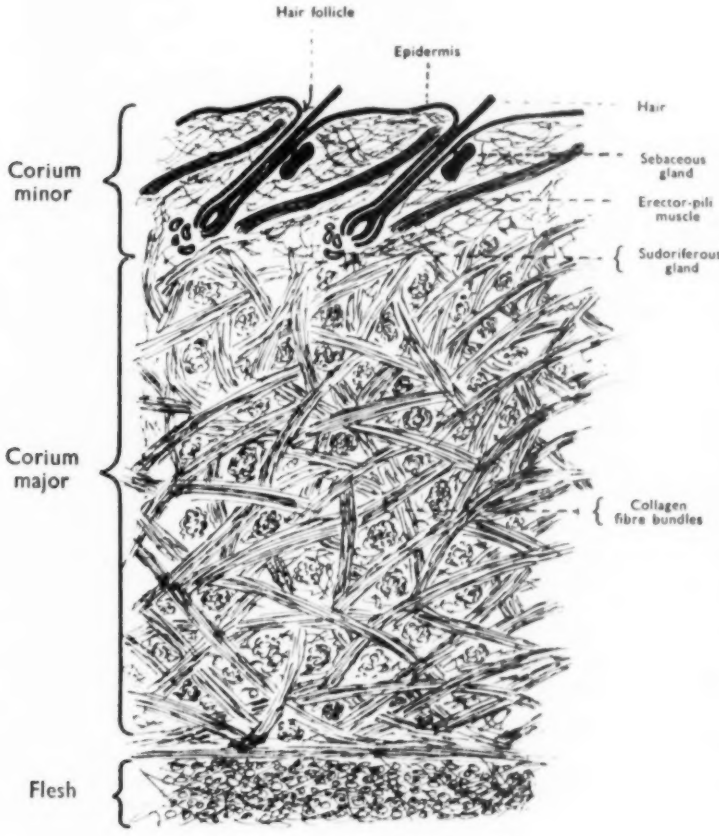

FIG. 1.—Diagrammatic Section of Ox Hide

of cationic or basic dyes on untanned collagen, and found that pelts will dye quite well and regularly with cationic dyes, but in the case of vegetable-tanned leather the presence of vegetable tannins causes increased combination and less penetration of basic dyes. The behaviour in dyeing of leathers tanned with combination tannages, where both types of side-chains are occupied to a greater or lesser extent with tanning agents, supports the Otto theory, inasmuch as this type of leather is generally difficult to dye a full colour.

5. DYEING REQUIREMENTS

(*a*) *Fastness to Wet and Dry Rubbing*

Leather to be worn or carried must always be fast to wet and dry rubbing, and this calls for careful exhaustion of dye liquors, the complete combination of dye with leather in a non-reversible reaction, and complete absence of marking-off tendencies. This particular property is complicated by the fact that, after being dyed, leather is nearly always treated with weakly alkaline fat-liquor emulsions, which can either loosen the dye or form soaps with it, giving rise to results which are not fast to wet or dry rubbing.

(*b*) *Fastness to Perspiration*

Leather to be worn, e.g. gloving, clothing, and hat leather, must be fast to perspiration, and to obtain this result on leather calls for the use either of cationic dyes or of laking techniques with anionic dyes, ordinary acid dyes being stripped by alkalis.

(*c*) *Fastness to Light*

The property of light fastness in leather dyeing is complicated by several factors. All leathers containing catechol or condensed vegetable tannins change colour by oxidation, generally turning pink or red, so that light-fast dyeings are impossible to obtain. Most leathers containing synthetic tanning agents yellow on oxidation, and again light fastness cannot be obtained. Most leathers contain oxidisable oils and greases, and again colour changes occur. When a leather is to be finally pigmented in finishing, then obviously light-fast dyeings are not so essential.

(*d*) *Fullness of Colour*

Leather should be dyed with a full surface colour. The intensity of surface dyeing suffers when methods are used to promote penetration, and in many cases a "topping off" or second dyeing is given after the through dyeing has been obtained. The same result can be obtained by using together two dyes of similar colour, one being a penetrating and the other a non-penetrating type. The fullness and brightness of colour are also often reduced because most leathers are coloured by the tanning agents, all vegetable-tanned leather being a shade of brown, while chrome leather is mainly a greenish white. Bleaching techniques are often employed before dyeing, but a white base is rarely, if ever, obtained, and the presence in the leather of residual bleaching agents, such as sulphur dioxide, can cause weakening and fading of the dyes used.

(*e*) *Penetration*

Leather is usually required to have a coloured cut edge, and, with the exception of white-backed leathers and shoe-upper grain leathers, the dyeing techniques are modified to give through dyeing. The penetration of dyes through leather is usually obtained by temporarily reducing the rate of combination between the leather and the dye. The rate of combination can be controlled by changing the polarity of the leather by change in pH; for example, addition of alkalis to bring the pH of the leather above 5·3 will reduce its affinity for anionic dyes. The reactivity of the protein can also be reduced by blocking the side-chain groups with tanning agents. The danger of this process is that the affinity for dyes is permanently reduced, and fixation problems can arise if the penetration is increased excessively by this method. A third method of obtaining penetration is to use homopolar dyes of good solubility and low molecular weight. In practice this type of dye gives good penetration on all tannages, but may be hard to fix. The manufacture of suède leather presents special penetration problems, because, after dyeing, the flesh surface is usually buffed or treated on a revolving carborundum-faced wheel, and the immediate surface actually removed; there should be no change in colour as a result of this operation. Unlevel colouring occurs if a mixture of dyes of unequal penetration rates has been used. The final complication of skin structure is, of course, always present, and varies from leather to leather, particularly when the thickness of the leather has been reduced by shaving or splitting. While penetration of a thin sheep skiver occurs readily, the penetration of cowhide, of, say, 2·5 mm. for case hide, is no easy matter. To summarise, the problem of penetration can be solved, but, after through dyeing, the production of a full surface colour and the obtaining of good dye exhaustion may be difficult.

(*f*) *Levelness of Colour*

The modern leather user, and the public in general, expect leather to be level in colour. With variation in the surface fibre density and porosity as well as surface blemishes, the level dyeing of leather is not easy. In general, levelness of dyeing can be obtained by careful liming and tanning, and by making sure that the surface of the skin is free from grease, soaps, and other compounds, such as calcium carbonate, which might exert a local action. In the dyeing process, levelness is obtained by careful control of the rate of fixation, and similar techniques are employed to those used to obtain penetration. The choice of dye is again of paramount importance, and for levelness of colour the dyeing rate should not be high. In practice, dye is often added in several portions to obtain levelness.

(*g*) *Fastness to Washing*

In the glove-leather industry, fastness of dyeings to washing is called for, particularly on oil- or aldehyde-tanned leather. The usual way in which such fastness is obtained is by the use either of metal-complex dyes or of chrome mordant dyes in

a metachrome type of process. With oil-tanned leathers sulphur dyes have been employed, and chamois tanners have also experimented with vat dyes, but on the whole the general practice is to mordant the chamois with a tervalent chromium salt and then to dye as for chrome leather.

6. DYES FOR LEATHER

The classes of dyes used on leather are varied. According to Hunnam[3] those azo dyes which come between the fast-to-milling and the level-dyeing acid dyes of the textile world are good leather dyes. He states that often an unlevel-dyeing wool dye is a very good leather dye. The early colouring of leather was done with natural dyestuffs. These all exert a tanning action and dye very level but dullish colours; the only three of any importance to-day are hematin, fustic, and brazilein crystals. These three materials are still employed when levelness of colour is important, and they can be used combined with acid or direct dyes, or as a base for basic-dye toppings. With a renewed demand for level-dyed leather with a top finish free from pigment, it is feasible that there may be a return to natural dyestuffs. That this demand has started can be seen from the enthusiastic reception of modern coachhide travel goods.

Basic dyes are employed for dyeing vegetable-tanned leather and mordanted chrome leather. In the former case, all the loose tannin is first rendered insoluble by the addition of tartar emetic, potassium titanium oxalate, etc. in order to prevent precipitation of the basic dye in the dyebath. The chief merits of basic dyes on leather are firstly that they give full, rich, powerful surface dyeing, and secondly that the dyeings are fast to perspiration, an important consideration in the dyeing of clothing and gloving leathers. The disadvantages of basic dyes are firstly their poor light fastness, secondly their tendency to bronze if used in excess, and thirdly the fact that they are generally difficult to use and control. Basic dyes have received a new lease of life with the introduction of cationic dyeing auxiliaries and a technique employing tungstophosphoric acid for increasing light fastness.

Acid dyes find wide application in the dyeing of all kinds of leather. As a class they penetrate fairly well in neutral or alkaline solutions, and subsequent acidification brings about combination with the leather. They give moderate-strength grain dyeings of reasonable levelness and light fastness; only in the case of full chrome leather is it necessary to employ restraining techniques for levelness.

Direct cotton dyes are used for surface dyeings on chrome leather, for which they have good affinity without acidification. As a class their light fastness is very good, and with only a few exceptions they give full surface colours. Many of the direct dyes also find a use in the dyeing of vegetable-tanned leather, in which case they are applied in the same manner as acid dyes. Direct Black BH (*C. I.* 401) is used in diazotisation dyeing processes for producing black and navy blue suède leathers.

7. DYEING METHODS

The method of dyeing leather is generally governed by the physical and chemical stability of the leather in question. Leathers of low tensile strength, e.g. sheepskin grain split or skiver leather, are usually dyed in a wooden paddle, a semi-cylindrical vessel fitted with a rotating blade. Ordinary sheep, calf, or goat leathers are dyed in a wooden drum, a rotating cylindrical vessel containing sufficient dye liquor to ensure its even distribution over the leather. Leathers which are required to be coloured on one side only are either brush- or spray-dyed on the appropriate surface. They may also be dyed by immersion on the surfaces only; one surface is subsequently removed during the finishing processes, which exposes an undyed face.

The temperature of dyeing is governed by the stability of the tannage; for vegetable-tanned leathers the usual temperature is 40°C., while for chrome leather it lies within the range 60–70°C. The prolonged boiling of leather is not feasible, for time as well as temperature affects the stability.

The pH ranges used also vary with the tannage. In the case of vegetable-tanned leather, the pH at the beginning of the dyeing may be approx. 5, and may be lowered to around 3·5 after the required penetration has been obtained. Full chrome leather is normally dyed above its isoelectric point in order to restrain combination between the leather and anionic dyes, starting at pH 6·5–7·0 and finishing at around pH 4·0. The pH adjustments are generally made with either ammonia or formic acid, both volatile substances which tend to leave the leather during subsequent drying and finishing processes.

When a high degree of penetration is wanted, concentrated dyebaths are used; for maximum levelness, on the other hand, the addition of the dye in several portions is general practice. For full surface colouring a so-called sandwich process of dye and acid is used, the first portion of dye being allowed to penetrate and then being fixed by acidification, and the second addition of dye being subsequently fixed mainly on the surface. Full surface colouring can be obtained also by topping-off dyeing processes, or by using a mixture of penetrating and non-penetrating dyes of similar colour. The presence of a large quantity of neutral salts, either dye diluents, added salts, or water hardness, is not desirable, as they tend to reduce the solubility of dyes or they may crystallise out on the leather surfaces during drying.

The quantity of dye is calculated either on the weight of leather or on the area of leather, the latter method giving more easily reproducible dyeings. The dyeing of leather to match a given pattern is a skilled and difficult process, particularly when glazed or pigmented patterns are encountered. The use of dyeing formulæ in leather dyeing calls for the intelligent use of recipes and patterns, and, of course, the difficulty of supplying the leather dyer with a uniform raw material has already been emphasised.

8. DYEING AUXILIARIES

The use of auxiliary products in leather dyeing is now general practice, and when the auxiliary and the dye carry the same electric charge a restraining effect occurs, giving greater levelness and penetration. When auxiliary and dye carry opposite

charges, then increased fixation with fuller surface coloration occurs. The two main types of auxiliary are surface-active materials and synthetic tannins. When ionisable wetting agents are used in dyeing, it is found that the waterproofness or water repellence of the leather is permanently reduced, a serious disadvantage in many instances. The use of synthetic tannins can change the feel or handle of the leather, and they tend to reduce permanently the reactivity of the leather by occupying the vacant side-chain groupings. In many ways the use of auxiliaries calls for extreme care if harmful results are to be avoided. The advantage of using pH changes for this type of effect is that they are controllable, and any specific action can be stopped at any time during dyeing. We do not, however, wish to give the impression that we are "agin auxiliaries", but "forewarned is forearmed".

9. PIGMENT FINISHING OF LEATHER

To complete the survey of leather coloration it is necessary to consider the use of pigmented films or "dopes". At the present time a very high proportion of dyed leathers are pigmented on the surface to some degree, and, more often than not, looseness of colour on finished leather arises from the surface pigmentation and not from the dyeing, as is commonly supposed. The practice of pigment-finishing leather has arisen from the demand by leather users for unnatural levelness and brightness of colour. The adoption of mechanical mass-production techniques by the footwear and leather-goods manufacturer, in place of the old hand cutting and sewing operations, has meant that leather has to be uniform in all its properties, for one main advantage of leather substitutes, which can be sold by the roll, is their uniform character. Thus there has been a tendency for leather to imitate its imitations, a foolish position for any industry to get into. The use of pigmented films of high opacity does enable the leather finisher to obliterate many of the lighter grain defects. This fact is of considerable economic value to the leather dresser, particularly under conditions such as those ruling today, with rising raw hide and skin prices on the one hand and considerable consumer price resistance to leather articles on the other. We are more than ever faced with the problem of producing a silken purse from the sow's ear.

The pigmented film is applied by brush, pad, or spray, in the form of pigment, binder, plasticiser, and a suitable aqueous solution. After the application of the pigmented film, the leather may be given a non-pigmented film which, together with the binder in the pigmented film, can be fixed or rendered insoluble by the application of heat, pressure, or both. Alternatively, the finish may be fixed by chemical action on the binder; e.g. a casein binder when sprayed with formaldehyde or chromium salts becomes practically insoluble in water.

The pigments used in leather finishes are of four types with widely varying properties—

Firstly there are the natural earth pigments, e.g. iron oxides; when used on leather this type of pigment gives a film of high opacity, moderate tinctorial strength, and poor texture. This group of pigments is mainly employed for brown colours of all shades, particularly tan browns and orange browns. The difficulties encountered with them are the somewhat painted, artificial appearance they give to the grain if used in excessive quantity, and their coarse particle shape, giving thick films in use.

The second group of pigments comprises the inorganic pigments, such as titanium dioxide and the lead chromes. These have a higher tinctorial strength than the natural earths, and their opacity is quite high. Provided their specific gravity and particle size and shape are suitable, these materials can be used to give reasonably good leather finishes of good colour and texture.

The third group of pigments are the colour lakes, both toner lakes and normal lakes being used in leather finishes. This type of pigment gives a film of moderate or high tinctorial strength and poor opacity. In practice their poor opacity can be increased by introducing white pigment covered with a suitable dye solution or by reducing the total light reflectance of the finish.

The organic pigments or insoluble dye types constitute the fourth group, and these have good tinctorial strength and moderate to poor opacity. These are mainly used for blues and greens.

The pigments used in leather finishes must be completely inert chemically, especially towards the leather and the chemicals it may contain. They are generally ground and dispersed in oil, and supplied to the leather finisher in concentrated pastes, semi-pastes, and liquid finishes containing in addition a proportion of binding material. The particle size of the pigments is very important, the smallest particle size consistent with reasonable opacity being used; 1–10 μ. is the usual range of particle sizes.

The binding medium is designed to give a transparent film with good adhesion to the leather, providing a continuous phase in which the pigment and other film ingredients are dispersed. It should be capable of being insolubilised or should itself be insoluble in water. There are three main types of binding media used for leather finishes— protein binders, cellulose nitrate, and synthetic resins.

The first group consists of casein and egg and blood albumen. The casein films have the best binding power, while the albumens provide a harder film which can be friction-glazed to a high gloss. All these materials require the addition of a sulphated-oil plasticiser and all can be rendered insoluble with formaldehyde and chromium salts. The protein-bound films all have a reasonably good handle and are used for leathers which are friction-glazed to a high polish. The main disadvantage of this type of film is that it is impossible to make it completely fast to wet rubbing, particularly in alkaline solutions.

The earliest types of pigmented film to be completely fast to water were bound with cellulose nitrate applied in solution in suitable solvents and diluents, and for many years this process played an important part in leather finishing. Today the use of this type of film is being slowly abandoned in favour of films bound with synthetic resins. The main leathers still finished with cellulose nitrate

lacquers are upholstery hides and certain leathers for handbags and travel goods.

The use of acrylate and methacrylate resin emulsions was started in Germany in the 1930s, but since the 1939–1945 war the finishing of leather with resin emulsions has made great strides, made possible by the increased availability of resins. Two typical resins used for leather finishing are based on (i) ethyl acrylate, which yields soft elastic films, and (ii) butyl methacrylate, which yields harder elastic films. Used alone, these resins give completely insoluble films which can be heat-treated to give a reasonably high gloss. As the quantities of pigments, waxes, etc. are increased in the film, its fastness is gradually reduced, so that in resin finishing one or two coats of different composition are given, the top film being a hard resin with as little film adulteration as possible. The danger with this type of finish is that, if it is applied too heavily, the inherent character of the leather may be lost.

The plasticisers used in leather finishes are mainly sulphated oils and glycols. Their function is to keep the film flexible and elastic, the problem being to prevent the plasticiser from being absorbed by the leather. This can be done firstly by previously fat-liquoring the leather with oils, and secondly by using plasticisers of high molecular weight.

Finally, the finish is diluted for use, with solvents and diluents in the case of cellulose nitrate, and with water or synthetic-dye solutions for the aqueous finishes, the concentration varying with the porosity of the leather and the thickness of the film required.

10. CONCLUSION

In conclusion we would like to express the opinion that the coloration of leather is becoming increasingly a science rather than an art, and the modern leather colourist is looking more and more to the scientist to provide him with the means of keeping alive the old saying—"There's nothing like leather."

(*MS. received 29th June 1953*)

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The Structure and Chemical Properties of Dyes in relation to their Use

T. VICKERSTAFF

Meeting of the Summer School held in Loughborough College on 26th August 1952, Dr. D. Starkie in the chair

Before the discovery of synthetic dyes, the art of dyeing was really a triumph of man over Nature. Obstinately insoluble dyes were crushed and squeezed from vegetables and insects, dissolved by chemical processes which were but vaguely comprehended, and applied to fibres for which in many cases they had little affinity. It is, indeed, a wonder that successful dyeing was achieved at all.

When synthetic dyes were discovered their dyeing properties, again, were largely a matter of chance, and it is fortunate that the chemical constitution of Perkin's Mauve was such that it had enough affinity for natural fibres to be recognised as a dye. But this stage has now passed. Our knowledge of the constitution of dyes is vastly greater than it was in Perkin's day, but more important, perhaps, we now have a much better understanding of the mechanism of dyeing. It is now realised that dyeing is a process of interaction between the dye and the fibre and that, although this process is an adsorption phenomenon, it is clear that the chemical constitution of both the dye and the fibre must determine whether combination between the two will take place and what the properties of the resulting combination or dyeing will be.

It is doubtful, however, whether this fact was thoroughly appreciated by chemists in the early days of the dye industry. Chemists at that time were too enthralled with the discovery that they could make coloured organic molecules and were fully occupied with trying all the variants of intermediates which they could find and ranging over the colour gamut, to bother about the dyeing properties of their compounds. Only with the discovery of the direct cotton dyes was the importance of chemical constitution in controlling dyeing behaviour driven home to dye chemists, and even now the full implications have not been exhausted. The constitutions of the great majority of the dyes used today are determined by manufacturing considerations such as the intermediates which are available, and not by a consideration of what groups should be present in the dye molecule to yield desirable dyeing properties. This does not, of course, imply that all these dyes are unsatisfactory—merely that some of them are. It is true to say, however, that, with the broad requirements of the dyeing trade already filled, the successful introduction of any new dye is increasingly dependent on improved dyeing behaviour or fastness properties, and consequently there is an increasing tendency to consider the constitutions of dye molecules with this end in view.

The constitutions of existing commercial dyes, which are all successfully applied to textile fibres, are so varied that at first sight it seems impossible to trace any detailed connection with dyeing. One feature which stands out clearly, however, is the importance of ionic charge. Since dyes are still applied almost exclusively from aqueous solution, solubility in water is an essential property. By far the most powerful solubilising groups are those which ionise in water, and so most dyes contain one or more ionic groups. Thus the acid dyes usually contain sulpho or carboxyl radicals, the

vat dyes ionised phenolic radicals, and basic dyes cationic quaternary ammonium radicals. The existence of an electrical charge on the dye molecule has a very great effect on dyeing behaviour, as will be seen later.

Although ionic effects are the most obvious, other structural features and other substituents in dyes also affect dyeing. The relative importance of ionic charge and general structure differs according to the fibre being dyed. At the one extreme are the animal fibres, where the charge on the dye molecules is of outstanding importance, compared with which other structural features, apart from mere molecular weight, have a trivial effect. Indeed, almost any organic molecule which will ionise in aqueous solution can be adsorbed to some extent on wool under suitable conditions. Not so, however, with cellulose fibres, where the effect of charge is of a secondary order and the molecular architecture of the dye of paramount importance. In the cases of cellulose acetate and especially the newer synthetic fibres—Terylene polyester fibre and Orlon—electrical charge again becomes a primary consideration, but this time in the opposite sense, for it appears that few compounds which are ionised can be absorbed by these fibres at all. In the rest of this paper these two factors of dye design will be considered separately.

Considering first, then, the general structure of the dye molecule, this is most critical in cellulose dyeing. In order to dye cellulose without mordants, direct cotton dyes must conform to a rigid specification, which is now fairly well known. It was Meyer [1] who suggested that the dyeing of cellulose was an adsorption process in which the dye molecules laid themselves alongside the cellulose molecules. The further study of this suggestion by Hodgson [2], Schirm [3], Rose [4], and others has led to the conclusion that, in order that a dye may have affinity for cellulose, the molecule must be capable of taking up a linear and planar configuration, and should contain hydrogen-bonding groups, preferably spaced some multiple of 10·3 A. apart. It should contain a long chain of conjugated bonds, and the minimum number of solubilising groups, preferably arranged along one side of the dye molecule. The evidence is strongly in favour of a lock and key process of adsorption, with the dye carefully built to fit the cellulose molecule.

In contrast to this, the effect of constitution in wool dyes is difficult to detect. For example, one common intermediate which is used for the preparation of a typical milling dye of high washing fastness is benzidine-2:2′-disulphonic acid, which cannot possibly result in a planar dye molecule. Evidently planarity is not essential, nor can any other features be selected as having real significance, with the exception of molecular weight. The early acid dyes were all of a very simple monoazo type, but it was soon observed empirically that polyazo compounds gave dyes of much higher wet fastness on wool. It ultimately became apparent that this effect was largely due to the increase in molecular weight, or rather decrease in solubility, for if the molecular weight is increased without alteration of the number of solubilising groups the wet fastness is increased, but if then a further sulphonic acid group is introduced, the fastness is decreased. This observation is pushed to its logical conclusion in the Carbolan (ICI) dyes, which are merely acid dyes in which the molecular weight has been increased and the solubility decreased by the introduction of large alkyl groups. Recently Meggy [5] has developed this theme by suggesting that the affinity of acid dyes for wool is largely due to the fact that the bulk both of the dye molecule and of the wool fibre is hydrophobic, and that, on dyeing, the two hydrophobic surfaces can come together with a reduction in potential energy. There does appear to be a considerable amount of truth in this theory, for Lemin [6] has examined the affinity of two series of azo dyes containing aliphatic chains, and has shown that the affinity increases by roughly 400 g.cal. per CH_2 group. In a series of substituted aniline→N.W. acid derivatives, also, Lemin demonstrated a correlation of affinity with molecular weight which seems to be relatively independent of the nature of the substituents (Fig. 1). No definite evidence of interaction of dyes

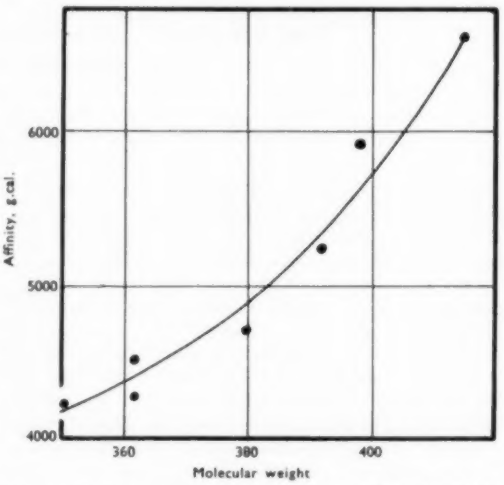

FIG. 1.—Relation between Affinity for Wool and Molecular Weight in a Series of Substituted 4-Hydroxy-3-phenylazonaphthalene-1-sulphonic Acids

with chemical groups in wool apart from ionic groups has yet been obtained, but some such interaction involving hydrogen bonding must occur, even though the effect is of a small order; for if this were not so, all dyes of the same degree of sulphonation should vary in wash fastness in direct proportion to their molecular area. In other words, the forces linking acid dyes to wool are, in order of importance—(i) ionic forces between the ionised groups of opposite charge in the dye and in the fibre, (ii) van der Waals forces between the hydrophobic parts of the dye and the fibre, varying with the area of the dye molecule or approximately as the molecular weight, and (iii) co-ordination forces or hydrogen bonds between specific groups in the dye and the fibre. Although evidence for the existence of the last-named forces

is lacking with wool, it should be noted that Klotz and Ayers[7] have shown that, in the interaction of aminoazobenzene with bovine serum albumin, linkage to the hydroxyl group of the tyrosine in the protein is involved, for on iodination the hydroxyl group is surrounded by iodine atoms, which act as an effective steric hindrance to approaching molecules and greatly reduce the adsorption of aminoazobenzene. The relatively minor rôle of such specific interaction is clearly shown by the smooth curve obtained when the affinities of a number of monobasic acids of differing constitution are plotted against molecular weight (Fig. 2).

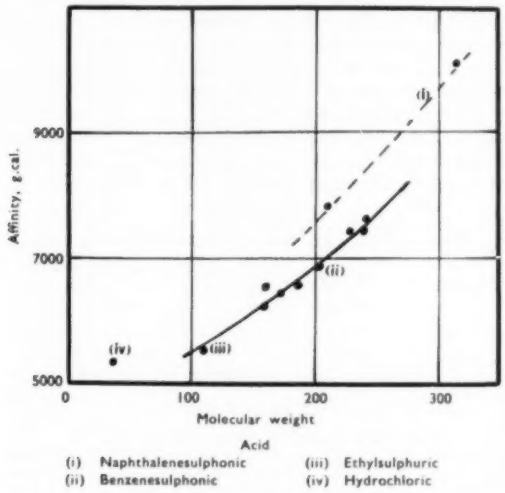

FIG. 2.—Relation between Affinity and Molecular Weight of Monobasic Acids on Wool

In the case of vat dyes on cellulose, it is again difficult to identify the structural features which contribute to the affinity, and it seems probable that van der Waals forces proportional to the molecular area are the most important. Thus in Fig. 3 is shown the correlation between the molecular weight and the affinity for cellulose of a large number of anthraquinone derivatives mainly of the substituted aminoanthraquinone type, as determined by Peters and Sumner[8]. It will be seen that there exists a fairly clear relation between the two factors. Apparently, however, planarity in the dye molecule is still a desirable attribute, for seven of the compounds which fall well below the mean line, i.e. have lower affinities than their molecular weights would suggest, carry *ortho* substituents in the benzoyl radical, which will have the effect of forcing the phenyl group out of the plane of the anthraquinone residue. The spacing of the quinone groups in the vat dye molecule seems to have little significance, for in a series of dyes consisting of two anthraquinone groups linked by an aliphatic chain no significant variation in affinity was noted as the chain was increased from four to ten carbon atoms.

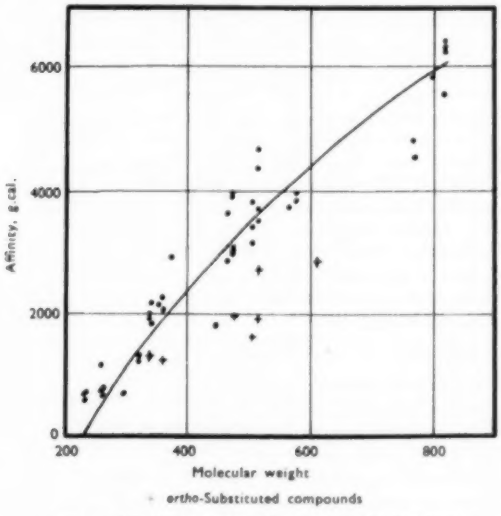

FIG. 3.—Affinity of Aminoanthraquinones for Cellulose

Turning to the question of ionic charge, this is clearly of importance in the dyeing of proteins with acid dyes, for, as is well known, the dyeing of wool in acid solution is largely an ionic process. Hydrogen ions are adsorbed from the solution, and then anions are taken up to produce electrical neutrality. The fact that dyes are adsorbed to a greater extent than inorganic anions indicates the presence of additional attractive forces between dye and fibre, which must be the van der Waals forces and co-ordination forces between reactive groups. In the case of level-dyeing acid dyes these non-ionic forces are relatively small in comparison to the ionic binding. Consequently, with such dyes, the maximum amount of dye which can be adsorbed is limited by the number of charged sites in the fibre. In the case of wool this is 0·8 g.-equiv. per kilogram, corresponding roughly to a 30% dyeing of a typical commercial dye. With nylon it is as low as 0·03 g.-equiv. or a 1% dyeing. The degree of sulphonation of a dye thus becomes critical in dyes for nylon, for, although it may be possible to apply 1·5% of a typical monosulphonated dye, a trisulphonated dye of the same basic structure would give a maximum of 0·5%. In other words, polysulphonated dyes will not build up to heavy shades on nylon. To a lesser extent the same problem is encountered on silk.

If wool is immersed in neutral or slightly alkaline solution it takes up a negative charge and consequently repels anions. If a dye is dependent for its affinity for wool on ionic forces, it will clearly fail to dye the fibre under such conditions. This is in fact the case with levelling acid dyes, and furthermore it can be shown that there is a close correlation between neutral dyeing behaviour and degree of sulphonation, monosulphonated dyes having a greater affinity for wool in neutral solution than have polysulphonated dyes. The electrical repulsion can be overcome if the dye has considerable non-ionic affinity for the fibre, as in the milling and Carbolan dyes, and it has been shown that with such dyes the saturation value of wool is higher than the electrical equivalent. The nature of the electrical effect is clearly shown by the action of

TABLE I

Dye	Mol. Wt.	Basicity	Levelling
Sulphanilic acid→1-naphthol	328	1	5 (good)
Sulphanilic acid→1-naphthol-4-sulphonic acid	408	2	4
Sulphanilic acid→1-naphthol-3:6-disulphonic acid	488	3	3–4
Sulphanilic acid→1-naphthol-3:6:8-trisulphonic acid	568	4	3
Aniline-2:5-disulphonic acid→1-naphthol-3:6:8 trisulphonic acid ...	648	5	2
Aniline→1-naphthol-4-sulphonic acid	328	1	5
Aniline→1-naphthol-3:6-disulphonic acid	408	2	4–5
Aniline→1-naphthol-3:6:8-trisulphonic acid	488	3	3–4

neutral salts in dyeing. In acid solution addition of salt reduces the amount of dye take-up, as the inorganic anions displace dye anions from the fibre. In neutral solution, inorganic salts promote dyeing by screening the electrical charge on the fibre. A beautiful illustration of this is described by Preston [9], in which wool dyed with a Carbolan dye from acid solution is shown to have a relatively hydrophobic surface whereas when dyed from neutral solution the fibre surface is hydrophilic.

The charge on the acid dye anion appears to play a part also in determining kinetic behaviour. Townend [10] studied the rate of dyeing of the following three dyes of the same basic structure—

Naphthalene Red J...	... Monobasic
Naphthalene Red EA	... Dibasic
Naphthalene Scarlet 4R	... Tribasic

and showed that the rate of dyeing increases with decreasing sulphonation. Fern and Valentine [11] have confirmed this observation and have found that the pair of dyes Naphthalene Orange G and Naphthalene Fast Orange 2G behave in the same way. Abbot has observed microscopically that, with dyeings of the above three dyes on nylon monofil, the extent of penetration is inversely proportional to the basicity. These observations can be explained on the basis that polybasic dyes, at an equivalent surface concentration in the fibre, are at a lower molecular concentration, so that the concentration gradient governing rate of dyeing is greater with monobasic dyes than with polybasic dyes. Furthermore, it was shown by Gilbert [12] that the introduction of a sulphonic acid group into a dye molecule increases its affinity considerably, so that the polybasic dye will have a much higher exhaustion than the monobasic, and will be more firmly attached to the fibre and less likely to diffuse. This is confirmed by other observations of Townend [10], in which he found that, in several series of dyes of increasing basicity, levelling decreases with increasing sulphonation (Table I). This is directly contrary to the conclusion of Speakman, although it must be noted that the latter never carried out any practical levelling tests. Townend was able to use the different dyeing rates of mono- and poly-sulphonated dyes to develop two-tone dyeing of normal and chlorinated wool in one bath, for with the slowly diffusing polybasic dyes any opening of the wool structure, as by chlorination, greatly favours diffusion into that fibre as compared with normal wool, thus giving a very great colour contrast, whereas with the monosulphonates the contrast is small.

In the case of cellulose the effect of electrical charge is not so evident at first sight. Cellulose fibres are all negatively charged in neutral aqueous solution, and so repel dye anions. Electrolytes facilitate the approach of anions to the fibre surface by screening the electrical charge, and thus promote dyeing. In complete absence of electrolyte, anionic dye adsorption is slight, but the dye itself can act as an electrolyte, so that at high dye concentrations some dyeing occurs with dibasic dyes but none with tetrabasic dyes. In other words, the tetrabasic direct cotton dyes are in general more salt-sensitive than the mono- or di-basic dyes. This is shown in Table II [13].

TABLE II

Mean Exhaustion of Direct Cotton Dyes on Cotton

Basicity	No. of Dyes	Exhaustion without Added Salt	Exhaustion with 200% Salt
2	16	32	85
3	5	17	90
4	7	12	85

Apart from the number of sulphonic acid groups in a dye molecule, it has been suggested from time to time that the dissociation constant of the group may be important. Elöd and Fröhlich [14] have recently claimed to have measured the dissociation constants of acid dyes and to have found a correlation with wet fastness, but we have been unable to confirm this.

From the foregoing it will be apparent that a knowledge of the constitution of dyes and particularly of their basicity can at times be of valuable assistance to the dyer, and it is possible, when fuller information is available in the Second Edition of the *Colour Index*, that further relations between constitution and dyeing behaviour may be uncovered.

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Radioactive Isotopes in Roller Printing

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Meetings of the Scottish Section held at the St. Enoch Hotel, Glasgow, on 23rd September 1952, Mr. R. D. Alexander in the chair; and of the Manchester Section held at the Textile Institute, Manchester, on 17th October 1952, Mr. F. Farrington in the chair

Of the many problems which beset the printer it is probable that the one which has caused more anxiety and loss than any other is that of colour soiling. The reason is that this fault is one inextricably bound up with the human element, and it has not been possible hitherto to apply any form of scientific or positive control.

Some years ago, one of us (W.M.) conceived the idea of obtaining such control by applying a labelling system based on radioactive isotopes. Suitable instruments were built, and gave satisfaction. We may first consider whether there is a real need for such a system, and if so, why other and possibly simpler methods of detecting and controlling colour soiling are less effective. To do this it is necessary to summarise briefly the factors which contribute to the occurrence of this fault.

The printing machine itself consists of a large cylinder round the circumference of which are arranged printing rollers in the sequence of the pattern. The printing roller is supplied with colour by a brush or roller furnisher which revolves in a colour box containing thickened colour. The box and furnisher are raised to a position such that the furnisher is in contact with the roller, the whole surface of which is supplied with colour. It is desired, however, to transfer only the engraved area from the roller to the cloth, and therefore the surplus colour must be removed from the plain portion. This is done by the doctor blade—a sharp knife-edge, rather longer than the roller itself.

Although the doctor blade continuously scrapes the roller free from colour, except where the latter is held in the engraving, it leaves on the plain surface a fine film which acts as a lubricant for the doctor edge, preventing wear and consequent streaks and scum. The transference of part of this film to following rollers helps in the build-up of contamination or soiling.

The machine cylinder is lapped with several thicknesses of cloth, referred to as *lapping*, and the cloth for printing travels round the cylinder, between it and the printing rollers. What is called a *back grey* is inserted between the printed fabric and the lapped cylinder. This back grey is wider than the printed piece, and takes care of the surplus colour. In printing, the cloth passes through the machine, receiving colour from each roller in turn, until the pattern is complete.

The colours are arranged in the machine so that, as far as possible, in no case will a colour be capable of visibly contaminating the colour following it; but it is not always possible to provide for this, for a variety of reasons.

The cloth and the back grey carry forward surplus colour, which, by pressure of the nips, is transferred to the surface of the following roller, and from there, via the furnisher, to the colour box. This is the chief source of contamination.

If the degree of such contamination is not significant, the situation is normal and the printer is occasioned no anxiety. If, however, there is sufficient contamination to cause visual soiling, the printer is placed in a very difficult position. In this case he has to rely on skill and experience to know when to take action, which he does by removing part of the colour from the box and replenishing with fresh colour. By misjudging in one direction he will produce soiling, and by misjudging in the other direction he will cause extravagant waste of colour.

He can check the effect of whatever action he takes by the lengthy process of developing and washing cuttings off his running, but during the time taken to do this upwards of 1000 yards of cloth can be spoiled.

Another means which printers sometimes adopt to detect colour soiling is to note the appearance of the colour box. It should be remembered, however, that many dyes, particularly vat dyes, are not identical in colour during the printing process and after development: the effects of soiling can be completely masked by the presence of leuco vat dye in the box. Only under favourable conditions, therefore, as when acid, direct, basic, or some chrome dyes are being printed, can this means be used for detection.

It would appear that there is a need for a more positive method of control, and the use of radioactive labelling seems to be the answer to this difficult problem. By such a method it is possible not only to detect contamination but also to measure it continuously and with accuracy.

The labelling technique depends upon the use of radioactive isotopes. These are unstable elements which decay spontaneously with the emission of α, β, or γ rays. The rate at which this decay takes place varies enormously with different elements, and is measured in terms of the *half-life* of an element, which is the time taken for that element to lose half its original activity.

Modern nuclear physics has made possible the preparation of radioactive isotopes in the atomic pile. Phosphorus 32, which is found to be most suitable for labelling in this technique of soiling detection, is prepared by bombarding phosphorus 31 with neutrons. Some of the atoms of phosphorus 31, under such conditions, capture one neutron and become atoms of phosphorus 32, which emits electrons. These electrons are capable of ionising air, or other inert gas, converting it from a non-conductor to a conductor of electricity. Advantage is taken of this in the construction of the Geiger

counter, which forms the measuring unit of the soiling-detection instrument.

The counter consists of a sealed glass tube containing a non-conducting gas. Fitted into this tube are two electrodes. If these are connected to the poles of a battery, no current will flow, but if the thin glass walls of the tube are exposed to fast moving electrons, the gas becomes ionised, and current, which can be measured, will flow. Since the conductivity depends upon the number of electrons producing the ionisation, and since this in turn depends upon the quantity of the source of radioactivity present, it is possible to measure the amount of the latter by measuring the electric current which flows.

It is important for the printer to know, not the quantity but the concentration of offending colour in his sensitive colour box. It is in fact this concentration which the instrument measures, for the following reason—

Phosphorus 32 emits fast moving electrons. These are easily absorbed by liquid or solid matter; that is to say, they lose their effect after travelling a very short distance through such obstructions. This means that the Geiger counter immersed in the sensitive colour box will respond only to the isotope label contained in a small and definite annular volume round its surface. In other words, it measures the concentration of label, and therefore of offending colour.

Phosphorus 32 was selected for the purpose because—

(i) It has a half-life of 14½ days, which is long enough for it to be practically useful, and yet not so long that accumulation can occur.

(ii) It emits only β rays, which are easily stopped by comparatively thin layers of liquid or solid matter, and therefore not only measures the concentration of offending colour, but also gives rise to no difficult problems of safety measures.

(iii) It can be produced with regularity in the pile, and supplies offer no difficulty.

The technique of applying isotope labelling to soiling detection is as follows—

The printer knows beforehand when he has a combination which is dangerous from the soiling point of view. He also knows which is the sensitive, and which the offending, colour. Samples of these two colours are tested in the laboratory, and the point is determined at which contamination first becomes visible. This is easily and quickly carried out by adding varying quantities of the offending colour to the sensitive colour, and the result is expressed in terms of a percentage of the former in the latter. This figure is referred to as the *soiling level*, and it usually lies between 0·1% and 1·0%.

When this has been done, the offending colour is labelled by adding to it a calculated amount of isotope, and checking on a monitor, which consists of a Geiger counter attached to a meter calibrated in terms of soiling level. From the colour mixer's point of view, all that happens is that he immerses the Geiger counter in the colour and reads off the figure indicated on the meter. If the predetermined level is 0·5%, for example, he adjusts the isotope addition up or down until the instrument indicates 0·5%.

This instrument is referred to as the *colour shop monitor*. It can be calibrated on any convenient strength of isotope, and it has been found that 100 microcuries per gallon of colour is a suitable strength for a soiling level of 1%. When the soiling level is high, the danger point is reached more slowly, and a smaller amount of label is required. When the level is low, the danger point is reached more quickly, and a larger amount of label is required. It has been found that this is in exact inverse proportion: i.e. 100 microcuries/gal. for a soiling level of 1·0% is equivalent to 200 microcuries/gal. for 0·5% soiling level, and 50 for 2%.

When the colour has been correctly labelled, it is transferred along with the other colours in the colouring to the printing machine, and here another instrument is installed. This one is equipped with two Geiger counters, and these are installed in the colour box of the sensitive colour. The sensitive colour is not labelled, and shows no radioactivity. When printing begins, therefore, the instrument registers nil. As printing progresses, contamination begins to occur, and radioactivity appears in the box of the sensitive colour. This is registered by the instrument, and the needle creeps round towards the danger line clearly marked on the instrument face. The printer takes action to check this by removing colour and replacing with fresh, and so long as he keeps the needle below the danger line no soiling will appear anywhere on his cloth.

It may be argued that the use of radioactive materials will give rise to misgivings on health grounds. Experience has shown these misgivings to be unwarranted. The amount of radioactive material finding its way into the effluent is many times less than the amount officially allowed for drinking water, and this margin is further increased by the fact that the isotope used has a half-life of 14½ days, so that accumulation cannot occur.

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The Development of the Geometric Staining Scale

K. McLaren

The various methods which have been proposed in different countries for evaluating the degree of staining of adjacent undyed material in fastness tests are reviewed. The most recent proposal, the geometric staining scale, is now being studied in several different countries and may become internationally accepted.

INTRODUCTION

When a sample of coloured material is subjected to a fastness test, it is usually necessary to determine to what extent adjacent undyed material is stained. The degree of staining can, of course, be recorded by the use of subjective terms such as "slight", "much", etc., and this was the method generally employed, e.g. in the first edition of the *Colour Index*[1]. Such subjective terms are, however, vague, and there have been two alternative methods proposed for recording the degree of staining with greater precision—the use of dyed standards and of fixed standards respectively.

DYED STANDARDS

The use of dyed standards was first proposed by the German Fastness Commission (Deutsche Echtheitskommission, D.E.K.) as long ago as 1914[2]. This method was to include three dyed standards (together with adjacent undyed material) with the patterns being tested. These standards represented the three major fastness grades—1, 3, and 5—in respect of both the effect on the pattern and the degree of staining. When the tests were completed, the samples under test were compared with the standards and assessed, two intermediate grades—2 and 4—being permitted. (Dyed standards were used also in the Society's original (1934) washing tests[3], but not for staining, for which no provision was made.)

This method remained valid in Germany until the end of the Second World War, when the original D.E.K. was disbanded.

FIXED STANDARDS

The dyed-standards method was very complicated—nearly 150 dyed standards were needed—and it was obvious that this degree of complexity was quite unnecessary. Consequently an alternative method—that of using fixed standards—was proposed independently in three different countries, a fact which supports the view that the new method was the only logical solution to the problem.

The fixed-standards method consists in comparing the results of fastness tests with patterns which define the various fastness grades but which have been prepared separately, once and for all, by dyeing or similar methods. Thus, for staining, the fixed standards would consist of five patterns of increasing depth, and if the depth of staining of adjacent white material were equal to that of standard No. 3, then the pattern under test would be rated 3 as far as staining was concerned.

The idea of using fixed standards was first conceived by the Society's Fastness Tests Committee in January 1940, but acceptance was deferred, as the testing methods themselves were under revision.

In 1942–43, Imperial Chemical Industries (Dyestuffs) Ltd. independently developed fixed standards, which were subsequently published in 1946[4]. For staining, they published fixed standards in nine different hues illustrating the five fastness grades ranging from Grade 5 (no staining) to Grade 1 (severe staining).

In 1943–44, the Swiss firm, J. R. Geigy AG., also independently developed fixed standards in sixteen hues very similar to the I.C.I. standards; these were subsequently published in 1947[5].

In 1945 the third independent development occurred in the U.S.A. The U.S. Quartermaster Corps specifications[6] proposed the use of the Munsell grey scale for assessing the degree of staining in rubbing fastness tests. This suggestion is of particular interest, as it marks the first appearance of a single grey scale for assessing patterns of different hues, a principle which has now been widely adopted. This proposal was considered in great detail by the Research Committee of the A.A.T.C.C., which modified it by supplementing the grey scale with other Munsell scales of five different hues. The resultant A.A.T.C.C. chart was published in October 1945[7].

In 1946–47, the Society's Fastness Tests Committee examined in great detail the question of assessing staining in order to decide whether the A.A.T.C.C. standards in six hues should be extended to nine or ten or reduced to one (grey); the statistical analysis of over three thousand assessments conclusively proved that a single grey scale was not significantly inferior to standards in nine hues[8]. It must be emphasised, however, that in these investigations the A.A.T.C.C. chart was matched on cotton and augmented by the addition of undyed material to represent Grade 5; this was necessary, as the Fastness Tests Committee had always considered that it was both easier and more accurate to evaluate the *contrast* between stained and unstained material by comparison with a series of fixed contrasts than to attempt to assess the absolute colour value in the American manner.

This statistical analysis also proved that the I.C.I. and the augmented A.A.T.C.C. standards gave the same results even though they had been developed completely independently. In April 1948 the Society's first staining scale, Grey Scale No. 1, was produced experimentally[9]. This scale compared as follows with the other fixed staining standards—

(i) S.D.C. Grade 5 represented the "maximum degree of staining which is allowed to be described as 'virtually unstained'", and the A.A.T.C.C. Grade 5, although not illustrated, was similarly described as "practically unstained"; in the I.C.I. and Geigy systems, however, Grade 5 was

completely unstained, any just perceptible staining being rated 4–5.

(ii) S.D.C. Grades 4 and 3 were identical with A.A.T.C.C. Grades 4 and 3.

(iii) S.D.C. Grades 2 and 1 were lighter than those of the A.A.T.C.C., as the S.D.C. scale was intended to be equally spaced according to Fechner's law, but the A.A.T.C.C. grey scale was equally spaced according to the Munsell Colour Atlas. This difference was, however, unimportant, as a degree of staining greater than Grade 3 is so serious that any minor differences in assessment would be insignificant.

In September 1949 the first of the Continental grey scales was described at a meeting of the Association des Chimistes de l'Industrie Textile in Lyons [10]. This had been prepared by the Swiss, and consisted of two identical sets of twenty-four patterns ranging from white to black. Although primarily designed for assessing the effect on the pattern, four of the greys were intended to be used for staining assessments, and represented Grades 4, 3, 2, and 1. In 1951 this scale was replaced by a similar scale containing only sixteen patterns; selected members of this scale, also, were intended to be used for staining assessments.

Geometric Grey Scales

In 1951 the Society's Fastness Tests Co-ordinating Committee (F.T.C.C.) accepted the principle that scales for assessing the effect on the pattern should not be equally spaced, or arithmetic, but should be geometric [11]. The Committee realised also that the reasons for this decision applied equally to scales for assessing staining; the Committee therefore prepared one such scale on cotton limbric, which was sent to the Continental and American Fastness Committees for comment in August 1951. For the production of geometric staining scales it was thought desirable to use the Adams "chromatic value" formula for computing small colour differences, as this had been found perfectly suitable for producing the scales for assessing the effect on the pattern [11]. The actual spacing selected for this geometric staining scale is given in Table I in "just

Table I

First S.D.C. Geometric Scale for Staining Assessment

Grade	Spacing (j.p.s. from white)
5	0
4	7
3	14
2	28
1	56

perceptible steps" (j.p.s.), the particular choice being made so that Grade 4 would be identical with the A.A.T.C.C. Grade 4; unfortunately, this particular construction resulted in a scale which was too widely spaced. This scale was sent to the Continental committees in spite of this defect, however, for the prime purpose of obtaining agreement on the adoption of the geometric principle; the accompanying memorandum pointed out its defects, and mentioned that a more suitable geometric spacing could be selected if necessary. The Continental committees, however, preferred an equally spaced or arithmetic scale, and one such scale had, in fact, been received by the F.T.C.C. at this time from Dr. P. Rabe of the German Fastness Committee, but it had been prepared on unbleached wool and the yellow colour of the higher grades was somewhat objectionable. In December 1951 the F.T.C.C. therefore prepared a similarly spaced, i.e. arithmetic, scale on bleached cotton, and submitted this to the Continental Committees.

The F.T.C.C. was not, however, entirely satisfied with this arithmetic scale, and in June 1952 it therefore considered in detail the question of a suitable spacing for the staining scale. The grey section of the A.A.T.C.C. scale consisted of four Munsell chips (Table II). The problem was to

Table II

Grey Section of A.A.T.C.C. Scale

Grade	Munsell Value
4	9
3	8
2	7
1	6

make a series of five contrasts by including one of zero contrast and using as many of the four existing A.A.T.C.C. standards as possible. The theoretical Munsell grey series ranges from white (Munsell value 10) to black (Munsell value 0) in ten visually equally spaced steps. The simple solution, therefore, would be to add a pattern of Munsell value 10 (for zero contrast), which would produce an equally spaced scale; unfortunately, however, patterns of this value (100·0% reflectance) cannot be produced commercially, the maximum value obtainable being about 9·6 (90% reflectance). Taking everything into consideration, the F.T.C.C. considered that there were three possible solutions—

(*a*) To take the existing A.A.T.C.C. standards for Grades 1, 2, 3, and 4 together with a Grade 5 of Munsell value 9·5; this scale is unevenly spaced in that the first interval (between Grades 5 and 4) is only half the interval between the other grades.

(*b*) To make Grade 1 equal to A.A.T.C.C. Grade 1 (i.e. Munsell value 6), to make Grade 5 equal to Munsell value 9·5, and to space the intermediate grades equally between them; this scale is spaced *arithmetically*.

(*c*) To make Grade 1 equal to A.A.T.C.C. Grade 1 (i.e. Munsell value 6), to make Grade 5 equal to Munsell value 9·5, and to space the intermediate grades *geometrically*.

Scales were prepared to illustrate these three possibilities, and the Committee unanimously selected the geometric staining scale. The colorimetric data for this scale are given in Table III,

Table III

Second S.D.C. Geometric Scale for Staining Assessment

Grade	Spacing (j.p.s. from white)		Munsell Value
	Theoretical	Actual	
5	0	0	9·38
4	4	4·2	8·98
3	8	7·8	8·60
2	16	15·8	7·76
1	32	31·8	6·02

from which it will be observed that Grade 4 as well as Grade 1 is identical with the corresponding A.A.T.C.C. grade; this was unexpected, but is another reason why this scale is the most attractive. The reason why the spacing differs so greatly from that of the first geometric scale (Table I), which was deliberately constructed so as to make Grade 4 equal to the A.A.T.C.C. Grade 4, is that the material used for Grade 5 of the first scale was bleached cotton limbric with a Munsell value of 9·66; in the second scale, pigment-coated white cards were used with a Munsell value of only 9·38. The F.T.C.C. now felt that, if no other staining scale had ever been proposed, this geometric scale would still have been selected out of all the possible alternatives, as its spacing closely illustrated the Committee's views on each grade.

Early in 1952, the Swiss–French–German Fastness Committees published a completely new edition of their provisional fastness tests [12], which included an illustration of two grey scales— one for the effect on the pattern and one for staining; each of these now consisted of five pairs of printed grey areas showing the five fixed contrasts, the general format being the same as that of the Society's Grey Scale No. 2 [13].

Later in the year, the actual scales themselves were received; these were prepared from dyed cotton and, although no measurements were made, the spacing of the staining scale appeared to be geometric; in October 1952, M. J.-P. Niederhauser of the French Committee reported that this scale was, in fact, geometric, although quite different in spacing from either of the two geometric staining scales described above.

Since that time, however, these Continental scales have been replaced, and the spacing of the latest staining scale has been found to be very close to the preferred spacing (Table III). It thus appears that the Continental Committees had independently reached the same conclusion regarding the ideal spacing of the staining scale.

The F.T.C.C. decided to bring all three possibilities (viz. unequal, arithmetic, and geometric) to the attention of the members of the Colour Fastness Subcommittee ISO/TC 38/SC 1 of the International Standards Organisation, and at the meeting in New York in November 1952 the preferred geometric scale (Table III) was accepted as a Tentative International Standard.

This Geometric Staining Scale [14] is to be used for staining assessment and for assessing the results of rubbing tests in place of Grey Scale No. 1 [9].

Methods for Making Grey Scales

The first grey scales prepared by the Fastness Tests Committee were made from piece-dyed textile material— bleached cotton for staining scales and unbleached wool for the "Effect on the Pattern" scales. When small colour differences are involved (Grade 4 of the "effect on the pattern" scale shows a contrast of only 1·5 j.p.s.), the patterns must be prepared with great accuracy, and it is extremely difficult to produce these in bulk by dyeing methods. Consequently, in February 1952, the F.T.C.C. approached the colour-printing firm, McCorquodale Colour Display Ltd., which had prepared the Hue Indication Chart for the Second Edition of the *Colour Index*. This firm developed a method for producing the scales with a high and reproducible degree of accuracy, as shown by the figures in Table IV.

Table IV

Geometric Grey Scale for Assessing the Effect on the Pattern

(Spacings of three preparations in j.p.s.)

Grade	Theoretical	First	Second	Third
5	0	0	0	0
4	1·5	1·7	1·75	1·5
3	3·0	3·3	3·3	3·0
2	6·0	6·3	6·4	6·1
1	12·0	12·1	11·5	11·3

It is interesting to note that, whereas the Society began with scales made from dyed textiles and transferred completely to pigment-coated card, the European Committees have done exactly the opposite.

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(*Received 4th June 1953*)

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COMMUNICATION

The Use of Non-ionic Level-dyeing Assistants with Chrome-complex Dyes

I. D. RATTEE

The factors involved in the absorption of chrome-complex dyes by wool and the problems arising in the search for level-dyeing assistants are discussed, with particular reference to the use of such non-ionic agents as Dispersol A (ICI), Lissapol N (ICI), Palatine Fast Salt O (IG), etc.

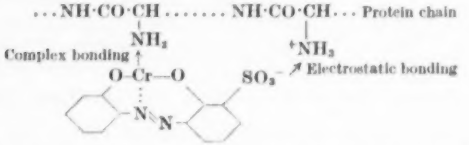
The reactions between Lissapol N and chrome-complex dyes have been studied. The formation of a complex between Lissapol N and chrome-complex dyes has been observed and measured quantitatively under controlled conditions. Complex formation appears to take place via the acid groups in the dye molecule.

It has been shown that the complex formation between the chrome-complex dyes and Lissapol N causes the latter to have a beneficial action in chrome-complex dyebaths, notably in the prevention of skittery dyeing.

A dyeing process has been developed, involving the use of 5% sulphuric acid, 20% Glauber's salt, and 1–2% Lissapol N on the weight of goods, which enables the acid addition to the dyebath to be reduced with minimum loss of levelling and the virtual prevention of skittery absorption. Comparisons are made between the new dyeing method and previously recommended decreased-acid methods which employed other agents. Lissapol N has been shown to be superior to other level-dyeing assistants for chrome-complex dyes from the points of view of greater effectiveness and greater ease of use because of non-frothing.

Introduction

The problem of the level application of chrome-complex dyes to wool is more complicated than that involved with level-dyeing acid dyes. This is due to their different mechanism of dyeing and fixation to the fibre, involving the formation of a co-ordination compound between the dye molecule and the wool. According to Ender and Müller [1] salt-link formation takes place between the acid groups in the dye molecule and the basic groups in the wool, and in addition complex formation takes place between chromium in the dye molecule and certain other basic groups in the wool. Measurements at saturation showed that one-tenth of the basic groups in the wool were involved in complex formation with chromium. Valkó [2] has developed a theory from these findings which suggests that complex formation takes place between chromium and amino groups in the wool—



Valkó suggests that chromium can co-ordinate only with unionised amino ($-NH_2$) groups and that the rôle of acid in the dyebath is to ionise these groups to ammonium ($-NH_3^+$) groups, thereby suppressing complex formation and enabling levelling to take place. This would be compatible with the particular shape of the pH–exhaustion curves previously reported by Lemin and Rattee [3], who found that, as the pH was reduced from 7, exhaustion increased to a maximum in the region of pH 2–3, and then fell again as the pH was further reduced. Moreover, marked levelling was observed only in the pH region lower than that giving maximum exhaustion. However, it is extremely doubtful whether primary amino groups exist in the wool molecule in acid solutions. It seems probable that the basic groups in wool which are involved in complex formation are secondary amino (>NH) groups in the side-chains from certain amino acids in wool. These groups are not normally charged in acid baths, but are known to develop a charge at low pH values. Thus the suppression of complex formation, and the levelling of chrome-complex dyes at low pH values, may be explained on the basis of the ionisation of the secondary amino groups at such pH values that they are unavailable for co-ordination with the chromium in the dye.

The absorption of chrome-complex dyes by wool may therefore be considered to be a resultant of three factors—

(*a*) Affinity of sulphonic acid groups in the dye for ionised basic groups in the wool (acid dyeing)

(*b*) Affinity of the positively charged chromium in the dye for acid groups in the wool (basic dyeing)

(*c*) Formation of co-ordination compounds between chromium in the dye and groups in the wool capable of participation in such compounds (complex formation).

The pH–exhaustion curves obtained by Lemin and Rattee [3] can be explained on the basis of these factors.

As the pH is reduced from 7 (neutral) the second factor— basic dyeing— gradually disappears, and may therefore be neglected. With decreasing pH the first factor— acid dyeing— causes increasing absorption up to a maximum, as with level-dyeing acid dyes. During this period complex formation between the dye and the wool may be regarded as proceeding without restraint, since very little if any ionisation of secondary amino (>NH) groups will occur. However, as the pH is further reduced, the secondary amino groups become ionised with a consequent reduction in the degree of complex formation. Thus the exhaustion decreases from a maximum.

No measurements have been made to determine the relative importance of these factors. It appears probable, however, in view of the fact that exhaustion is so markedly affected by suppression of complex formation at low pH values, that it is the third factor— complex formation— which exerts the greatest influence on the dyeing behaviour of chrome-complex dyes.

Thus it is not surprising that attempts to improve the levelling of chrome-complex dyes by

the use of anion- or cation-active levelling agents have met with little success as compared with the advances made in other fields by their use. Such agents are designed to compete with the dye ions for the fibre, and cannot be expected to affect the formation of co-ordination complexes between the dye and the fibre. The lack of marked improvements achieved by the use of these agents is not unexpected, although the possibilities of obtaining slight improvements are not to be ignored. In fact, use of such slight improvements has been made in the work here reported.

From theoretical considerations the ideal type of levelling agent for chrome-complex dyes would be a compound capable of co-ordinating in a readily reversible manner with either the secondary amino groups in the wool or the chromium in the dye. No such agent is known, however, other than the hydrogen ion that is at present employed.

The demand for levelling agents providing an alternative to the use of high acid concentrations arises from the deleterious action of the acid dye liquor on both the wool and the dyeing machinery. A fresh approach to this problem was indicated by the introduction of the level-dyeing assistants of the non-ionic type, e.g. Palatine Fast Salt O (IG), Dispersol A (ICI). These agents did not in any way affect the levelling of the dyes, but were claimed to improve their level-dyeing properties sufficiently for the acid addition to the dyebath to be reduced from 8% to 4%. The explanation of the beneficial action of these agents that has received the widest acceptance is due to Valkó [2], who, having observed complex formation between Palatine Fast Salt O and chrome-complex dyes, suggested that the agent must compete with the wool for the dye. However, such competition would imply a slowing down of the rate of dyeing or an increase in levelling or both. This has been found not to be the case [3].

Moreover, the value of these agents is disputed by many dyers, who are not able to derive any benefit from their use. The object of this present work was, therefore, to clarify the whole position and to determine the value of this type of agent. In view of the probable validity of Valkó's theory that the action of the agent is bound up with its ability to form a complex with the dye, attention has been paid to the question of increasing the degree of complex formation and the particle size of the aggregate. The work also extends to the determination of the best conditions for the use of non-ionic level-dyeing assistants in the application of chrome-complex dyes.

Experimental

1. LEVELLING PROPERTIES OF CHROME-COMPLEX DYES

Levelling tests were carried out on a number of chrome-complex dyes under different conditions of acidity by the well known mixed-liquor technique previously described [3]. In this experiment, as in all other dyeing experiments unless otherwise stated, botany-quality serge (warp 2-fold, 76 ends per inch; weft singles, 65–66 picks/inch) was employed. The material contained no free alkali.

This procedure was carried out with 1% shades of the standard-strength Ultralan (ICI) dyes with 8, 6, 5, 4, and 2% of sulphuric acid (98%) on the weight of wool (15 g.) added to the dyebath.

Results were obtained on a semi-quantitative basis by the preparation of standards representing the point of half levelness, i.e. 0·75% and 0·25% depth on the two patterns. Comparison between the dyed standards and the results obtained in the boiling-off test enabled the time of half-levelling to be estimated to within 15 min.

TABLE I

Approximate Times (min.) of Half-levelling of Chrome-complex Dyes under Varying Acid Conditions

Sulphuric acid (98%), % on wt. of wool	8	6	5	4	2
Ultralan—					
Yellow RS ...	40	55	55	>105	>105
Orange RS ...	85	85	85	85	85
Orange GS ...	25	55	55	>105	>105
Red RS ...	>105	>105	>105	>105	>105
Red BS ...	40	55	55	100	>105
Pink BNS ...	85	100	100	>105	>105
Bordeaux RS...	25	40	40	55	>105
Bordeaux BS...	40	55	55	85	>105
Violet 5RS ...	57	55	55	>105	>105
Blue 2GS ...	40	55	70	85	>105
Navy Blue BS	40	70	70	100	>105
Dark Green BS	70	85	85	>105	>105

It was clear from these results (Table I) that the levelling properties of many chrome-complex dyes were poor when 4% of sulphuric acid or less was employed. It may be concluded that it is unsafe to reduce the acid below 5% on the weight of goods.

The effect of Glauber's salt on levelling in the presence of 5% of 98% sulphuric acid on the weight of goods was determined by the same technique, 1% shades of the standard-strength Ultralan (ICI) dyes being used for testing (Table II).

TABLE II

Times of Half-levelling (min.) of Chrome-complex Dyes under Varying Dyebath Conditions

Sulphuric acid (98%), % on wt. of wool ...	8	5	5
Glauber's salt, % on wt. of wool	—	—	20
Ultralan—			
Yellow RS	40	55	55
Orange RS	85	85	55
Orange GS	25	55	40
Red RS	>105	>105	>105
Red BS	40	55	40
Pink BNS	85	100	85
Bordeaux RS... ...	25	40	40
Bordeaux BS... ...	40	55	40
Violet 5RS	55	55	55
Blue 2GS	40	70	55
Dark Green BS ...	70	85	85

2. REACTIONS OF NON-IONIC LEVEL-DYEING AGENTS WITH CHROME-COMPLEX DYES

A number of qualitative experiments were carried out with aqueous solutions of chrome-complex dyes containing the non-ionic level-dyeing

agents Dispersol VL (ICI), Dispersol A conc. (ICI), and Lissapol N (ICI)—

(*a*) A solution of 0·001 g. of Ultralan Blue 2GS in 50 c.c. of a 10% aqueous solution of Dispersol VL was maintained at 100°c. in a boiling water bath for 30 min. After this time it was observed that the colour of the solution had been lost almost completely. Examination in a collimated light beam showed that the Dispersol VL had formed loose aggregates containing concentrated dye.

(*b*) Dispersol A conc. (7 g.) was added to a solution of 0·001 g. of Ultralan Blue 2GS in 50 c.c. of water at 100°c. There was a marked loss of colour on dissolution of the Dispersol A, showing dye aggregation.

(*c*) A solution of 0·001 g. of Ultralan Blue 2GS in 50 c.c. of a 10% Dispersol A solution was maintained at 100°c. for 30 min. No change in colour was observed. On adding 5 g. of potassium chloride, the solution became cloudy and separated into two phases. The bulk of the dye was observed to pass into the upper (Dispersol A) phase.

(*d*) The previous experiment was repeated with a number of Ultralan dyes at the same concentration, starting at 20°c. with the potassium chloride already dissolved, and raising slowly to 100°c. The solutions were observed to become cloudy at 80°c., and to separate into two phases at 90°c. It was found that the dye was absorbed into the upper (Dispersol A) phase as follows—strongly in the case of Ultralans Yellow R, Orange R, Orange G, Red R, and Blue 2G; moderately in the case of Ultralans Pink BN, Bordeaux R, Dark Green B, and Navy Blue B; hardly at all in the case of Ultralans Bordeaux B, Red B, and Violet 5R.

(*e*) This last experiment was repeated using Lissapol N in place of Dispersol A and omitting the potassium chloride. Separation into two phases occurred very much more readily with Lissapol N. The dyes were observed to pass into the lower (Lissapol N) phase to a similar extent as into the Dispersol A phase in experiment (*d*).

The last of the qualitative experiments was put on a quantitative basis as follows—An aqueous solution was prepared containing 100 c.c. of Lissapol N and 1·6 g. of 98% sulphuric acid per litre. This solution was equivalent to a blank dye-bath containing 10% by volume of Lissapol N at a liquor ratio of 50 : 1. Two boiling tubes were filled each with 50 c.c. of the Lissapol N solution. To one tube 1 c.c. of a 0·5% aqueous solution of standard-strength chrome-complex dye was added. From each tube, 10 c.c. of solution was removed to be used as a standard. The two tubes were then lightly corked, and allowed to stand in a boiling water bath for 15–20 min. Under these conditions the Lissapol N was precipitated in the form of a coacervate, which coalesced at the bottom of the tube. The two tubes were removed from the bath and allowed to stand at atmospheric temperature for 12–15 hr. Ten cubic centimetres of the supernatant liquor from each tube was carefully removed. The four samples were then diluted to 50 c.c. with 50% pyridine. The optical densities of the two dye solutions were measured on a Hilger spectrophotometer as follows—

(i) The original dye solution against the original blank as standard.

(ii) The "cracked" dye solution against the "cracked" blank as standard.

This method of measuring the optical densities was employed in order to cancel out any optical density effects due to variations in the concentration of Lissapol N. By comparison of the two optical density values the percentage of dye absorbed by the Lissapol N phase was calculated. The experiment was carried out with a number of chrome-complex dyes, the degrees of complex formation obtained being shown in Table III. The percentage of dye removed by the Lissapol N phase may be regarded as a measure of the extent of complex formation between the dye and the Lissapol N under the specified conditions.

TABLE III

Complex Formation of Chrome-complex Dyes with Lissapol N

Dye	Complex Formation (%)
Neolan Blue GR (Ciba)	100
Neolan Red REG (Ciba) ...	96
Ultralan Orange RS (ICI) ...	94
Neolan Blue BR (Ciba)	94
Ultralan Red RS (ICI)	89
Ultralan Yellow RS (ICI) ...	84
Palatine Fast Blue BN (IG) ...	81
Neolan Flavine GFE (Ciba) ...	80
Ultralan Orange GS (ICI) ...	78
Neolan Pink BE (Ciba)	74
Ultralan Blue 2GS (ICI) ...	72
Neolan Yellow G (Ciba)... ...	57
Palatine Fast Green GN (IG) ...	55
Calcofast Wool Red GA (CCC)...	54
Neolan Red GRE (Ciba) ...	50
Palatine Fast Green BLN (IG)...	45
Neolan Yellow R (Ciba) ...	44
Neolan Violet R (Ciba)	39
Ultralan Pink BNS (ICI) ...	36
Neolan Violet 3R (Ciba) ...	33
Ultralan Dark Green BS (ICI)...	31
Neolan Green BG (Ciba) ...	20
Palatine Fast Yellow GEN (IG)	20
Ultralan Bordeaux RS (ICI) ...	19
Neolan Yellow 8GE (Ciba) ...	14
Ultralan Bordeaux BS (ICI) ...	5
Ultralan Red BS (ICI)	4
Neolan Bordeaux BE (Ciba) ...	0
Ultralan Violet 5RS (ICI) ...	0
Neolan Yellow BE (Ciba) ...	0

The effect of varying acid concentration on the complex formation of two dyes was measured at three acid concentrations by the technique described above. The results (Table IV) show little or no effect due to acidity.

TABLE IV

Effect of Acid Concentration on Complex Formation (%) between Lissapol N and Chrome-complex Dyes

Sulphuric acid (98%), g./litre	1·6	1·2	0·8
Ultralan Orange GS	75	81	85
Ultralan Bordeaux BS ...	3	0	8

The effects of increasing concentrations of both Lissapol N and dye on the complex-formation properties of two dyes was studied, the experiments being carried out with no modification of technique. In the first experiment the dye concentration was constant at 0·1 g./litre and in the second the Lissapol N concentration was constant at 100 c.c. per litre. The results are shown in Tables V and VI.

TABLE V

Effect of Varying Concentration of Lissapol N on Complex Formation of Two Chrome-complex Dyes

Dye	Lissapol N Concn. (c.c./litre)	Complex Formation (%)
ULTRALAN ORANGE RS ...	10	54
	20	71
	50	85
	100	94
	200	98
	400	98
ULTRALAN DARK GREEN BS ...	10	7
	20	16
	50	23
	100	37
	200	48
	400	60

TABLE VI

Effect of Dye Concentration on Complex Formation of Ultralan Dark Green BS with Lissapol N

Dye Concn. (g./litre)	Complex Formation (%)
0·04	23
0·08	38
0·12	45
0·16	44
0·20	49
0·24	48

These results show that the greater the concentration of dye or Lissapol N the greater the amount of complex formed. Complete absorption of the dye takes place only when the Lissapol N concentration is very high. Other methods of increasing the complex formation were therefore investigated.

It is known that various anions and cations affect the solubility of Lissapol N in water. The effects of a number of these ions on the complex-forming properties of Ultralan Dark Green BS with Lissapol N were measured. Seven solutions were prepared, each containing 100 c.c. of Lissapol N and 1·6 g. of 98% sulphuric acid per litre. Each solution contained one of the following electrolytes at a concentration of 0·1 M.— magnesium sulphate, lithium thiocyanate, ammonium thiocyanate, and sodium thiosulphate, nitrate, borate, and acetate. An eighth solution of Lissapol N and sulphuric acid was prepared without addition of further electrolyte.

The experiments were carried out with Ultralan Dark Green BS (0·08 g./litre), and also with Ultralan Violet 5RS (0·08 g./litre) and magnesium sulphate and lithium thiocyanate only.

From these results (Table VII) it is clear that sodium acetate and lithium and ammonium thiocyanates have a marked effect on the complex

TABLE VII

Effect of Various Electrolytes on Complex Formation of Two Chrome-complex Dyes with Lissapol N

Electrolyte	Complex Formation (%)
ULTRALAN DARK GREEN BS	
Sodium borate	4
Magnesium sulphate... ...	30
No addition	37
Sodium thiosulphate... ...	39
Sodium nitrate	43
Sodium acetate	66
Lithium thiocyanate... ...	75
Ammonium thiocyanate ...	79
ULTRALAN VIOLET 5RS	
No addition	0
Magnesium sulphate	0
Lithium thiocyanate... ...	0

formation between Lissapol N and Ultralan Dark Green BS. Of these, sodium acetate is the most readily available for dyehouse use, and accordingly its effect on the complex formation of a number of chrome-complex dyes was measured. Its action was found to be specific for Ultralan Dark Green BS, however (Table VIII).

TABLE VIII

Effect of Sodium Acetate on Complex Formation (%) of Chrome-complex Dyes with Lissapol N

Normality of sodium acetate	0	0·1
Ultralan—		
Yellow RS ...	83	84
Orange RS ...	95	94
Orange GS ...	90	89
Red RS	88	90
Red BS	0	0
Pink BNS ...	48	47
Bordeaux RS ...	21	27
Bordeaux BS ...	0	0
Violet 5RS ...	0	0
Dark Green BS ...	37	66
Blue 2GS	80	74

A number of experiments were carried out which were designed to indicate the mechanism whereby Lissapol N and presumably related non-ionic agents form complexes with chrome-complex dyes.

Firstly, measurements of complex formation were carried out with a number of the bases of chrome-complex dyes, i.e. the corresponding azo dyes before co-ordination with chromium. The dye solutions contained 100 c.c. of Lissapol N, 1·6 g. of 98% sulphuric acid, and 0·08 g. of dye base per litre (Table IX).

TABLE IX

Complex Formation between Lissapol N and Bases of Chrome-complex Dyes

Ultralan Dye Base—	Complex Formation (%)
Orange G ...	100
Red R ...	100
Pink BN ...	77
Red B ...	37
Blue 2G ...	100
Green B ...	100

A corresponding partition experiment with basic chromium sulphate (0·1 g./litre) showed that no chromium–Lissapol N complex was formed. In this case the green colour of the chromium salt was observed in the Spekker photoelectric absorptiometer.

Further experiments of a qualitative nature were carried out in order to investigate the behaviour of chrome-complex dyes with Lissapol N. Tests showed that Ultralan Blue 2GS and Ultralan Orange RS were completely insoluble in toluene even at the boil, and that addition of salt induced no partitioning of dye between a toluene–dye solution two-phase system. However, when 2·5 c.c. of Lissapol N was added to 25 c.c. of a 0·01% solution of Ultralan Blue 2GS containing 5 g. of potassium chloride, the dye–Lissapol N complex resulting from the "cracking" rose to the surface, and when a toluene layer was poured on to this system the complex passed into the toluene. The same behaviour was observed with Ultralan Orange RS. If the experiment was carried out without dye, so as to force the Lissapol N into the toluene, and then dye added, dye was observed to pass only very slowly into the toluene phase.

3. PROPERTIES OF NON-IONIC LEVEL-DYEING AGENTS IN THE WOOL DYEBATH

It has been previously reported that Dispersol A and Dispersol VL do not affect the levelling properties of chrome-complex dyes [3]. Whether this is the case with Lissapol N was investigated by the mixed-liquor technique [3] with 2% Lissapol N, 5% sulphuric acid (98%), and 20% Glauber's salt on the weight of wool. For comparison, levelling tests were carried out without Lissapol N, 1% shades of the Ultralan dyes being employed. The times of half-levelling by the two methods are shown in Table X.

TABLE X

Effect of Lissapol N on the Approximate Time of Half-levelling (min.) of Chrome-complex Dyes

Lissapol N, % on wt. of wool	0	2
Ultralan—		
Yellow RS	55	55
Orange RS	55	40
Orange GS	40	40
Red RS	>105	100
Red BS	40	40
Pink BNS	85	70
Bordeaux BS	40	40
Bordeaux RS	40	25
Violet 5RS	55	55
Blue 2GS	55	55
Dark Green BS	85	70

Clearly, Lissapol N was not capable of promoting greater levelling except in one or two cases, and was not markedly different in this respect from other non-ionic agents. The beneficial action of non-ionic agents must be due to another factor. Accordingly, attention was paid to the question of *skitteriness*, the term normally employed to denote marked fibre-to-fibre differences in a dyeing which cause effects variously described as "pepper-and-salt", "specky", etc. Although no real study has been made of this phenomenon, it is generally regarded as being due mainly to selective dyeing of different fibres or parts of fibres due to differences in damage. The test selected for estimating skitteriness was therefore based on the dyeing of chlorinated and normal wool in the same bath.

Patterns weighing 1 g. were weighed from acid-chlorinated and from normal wool delaine. Dual patterns weighing 2 g. were prepared by stapling together a 1-g. pattern from each material. Thirty 2-g. patterns thus prepared were boiled in water containing Glauber's salt (2 g./litre) to wet them out and to equalise any pH differences between the materials, which were then neutralised with sodium bicarbonate and buffered to pH 7. Two 1500-c.c. dyebaths containing 0·3 g. of chrome-complex dye and 2·4 g. of 98% sulphuric acid, one of which contained in addition 0·6 g. of Lissapol N, were prepared. These were equivalent to dyebaths containing 1% dye and 8% sulphuric acid (98%) with and without 2% Lissapol N on the weight of goods. The temperature of the two dyebaths was adjusted to 20°c., fifteen dual patterns were entered into each bath, and the temperature was raised by 2°c. per minute to the boil. When the boil was reached, a 2-g. pattern was removed from each bath together with 100 c.c. of liquor to maintain constancy of the liquor ratio. This was repeated every 5 min. for one hour.

A difference between the depths of dyeing on the two wools was observed in most cases, whether Lissapol N was present or not. However, the actual boiling time required to equalise the depths of shade was taken for purposes of comparison. It has already been shown that the effect of Lissapol N on the levelling properties of the dyes is small. The levelling taking place in order to remove the contrast between the two wools was, therefore, unaffected by the presence of Lissapol N, and it may be reasonably supposed that the time taken to remove the contrast is a function of the initial differences between the two wools.

The experiment was repeated using 5% sulphuric acid (98%) and 20% Glauber's salt with and without 2% Lissapol N on the weight of the goods. The reproducibility of this experiment is not high: although comparisons may be made between dyeings carried out side by side, reliable comparisons cannot be made between two sets of experiments. However, for the limited requirements of this work it was considered that the semi-quantitative test provided the necessary information. The results of these two sets of experiments are shown in Table XI. In this table, where the time taken to achieve levelness is given as zero, there was no contrast between the patterns on reaching the boil.

In the dyebaths containing 8% sulphuric acid on the weight of wool it can be seen that Lissapol N causes a reduction in the time required to achieve levelness with all dyes except Ultralans Red BS, Pink BNS, and Bordeaux BS. In the case of the Red RS, although levelness had not been achieved in a boiling time of one hour, examination of the patterns showed that removal of the contrast between the wools in the dyeings carried out in the

TABLE XI

Effect of Lissapol N on the Skittery Dyeing of Chrome-complex Dyes

(Time to achieve levelness, min.)

Sulphuric acid (98%), %*	8	8	5	5
Glauber's salt, %* ...	0	0	20	20
Lissapol N, %*	0	2	0	2
Ultralan—				
Yellow RS	35	0	>60	35
Orange RS	65	35	>60	40
Orange GS	45	20	>60	30
Red RS	>60	>60	>60	>60
Red BS	30	30	40	40
Pink BNS	0	0	>60	>60
Bordeaux RS	30	10	45	40
Bordeaux BS	45	45	>60	>60
Violet 5RS	35	30	40	40
Blue 2GS	30	20	>60	40
Dark Green BS ...	45	30	60	45

* % on wt. of wool

presence of Lissapol N was 30 min. in advance of that in the dyeings carried out in the absence of agent.

In the dyebaths containing 5% sulphuric acid and 20% Glauber's salt, improvement due to the presence of Lissapol N could be observed in all cases except those of Ultralans Red RS, Red BS, Pink BNS, Bordeaux BS, and Violet 5RS. In the cases of Ultralans Red RS and Pink BNS removal of the contrast between the wools was advanced 30 and 15 min. respectively by the addition of Lissapol N.

A further experiment was carried out to determine the relative values in preventing skitteriness of the three dyeing methods—5% sulphuric acid (98%) plus 20% Glauber's salt plus 2% Lissapol N, and 4% sulphuric acid with and without 4% Dispersol A. The experimental method employed was the same as before, 1% dyeings of two chrome-complex dyes being employed (Table XII).

TABLE XII

Relative Value of Three Dyeing Methods in their Effect on Skittery Dyeing

(Time to achieve levelness, min.)

Sulphuric acid (98%), %	5	4	4
Glauber's salt, % ...	20	0	0
Lissapol N, %	2	0	0
Dispersol A, %	0	4	0
Ultralan Orange RS ...	10	15	30
Ultralan Blue 2GS ...	10	10	30

Marked differences will be noticed between the values shown in Tables XI and XII for the times to achieve levelness with 5% sulphuric acid, 20% Glauber's salt, and 2% Lissapol N. This is due to the fact that the chlorinated wool used in the second series of experiments was less heavily chlorinated. The initial differences between the chlorinated and the normal wool and consequently the time taken to achieve levelness were therefore less than in the first series of experiments.

This Lissapol N method was tried out in bulk in order to test the validity of these findings. A three-colour mixture was dyed with Ultralans Yellow RS, Blue 2GS, and Red BS to a dull green on a piece in a winch machine. Cuttings were taken every 10 min. from the commencement of the dyeing. It was found that even after only 10 min. dyeing, when the temperature had reached 35°C., the dyeing was almost free from skitteriness, and that this even appearance continued throughout the dyeing to completion. It was observed that with Lissapol N no frothing or flotation took place in the dyebath, in marked contrast to the undesirable frothing occurring with Dispersol A. The effect of the level absorption markedly contrasted with that in a normal (8% sulphuric acid) dyebath, where considerable boiling was required to remove skitteriness. These results emphatically confirmed the basic correctness of the skittery dyeing test.

Since an important use of chrome-complex dyes is the level dyeing of carbonised goods, tests were carried out on specially prepared unevenly carbonised flannel using the reduced-acid methods employed in obtaining the results in Table XII. It was found in all cases that the covering of carbonising unevenness with chrome-complex dyes is unsatisfactory if the amount of acid employed is less than 8% on the weight of goods, and that the two agents tested had no effect in this respect.

Discussion of Results

The results in Table I demonstrate the marked loss in levelling power sustained by chrome-complex dyes as the dyebath acid content is reduced. The use of 4% acid definitely appears to reduce the levelling properties of the chrome-complex dyes compared with those of level-dyeing acid dyes, both measured by the mixed-liquor technique; when 5% of acid is used the levelling properties of the dyes are comparable with those of level-dyeing acid dyes such as Disulphine Blue ANS and Solway Blue 2GS, which are generally considered to be level dyeing. With 4% of acid in the dyebath, on the other hand, the levelling power of chrome-complex dyes drops to that of Naphthalene Scarlet 4RS and Naphthalene Black 12BS, which are known to cause trouble in all but heavy dyeings. Addition of 20% Glauber's salt to a chrome-complex dyebath containing 5% sulphuric acid on the weight of goods does not produce marked improvement, but is sufficient to raise the general standard of levelling properties to those of Solway Blue RNS or Azo Geranine 2GS, which are considered to be very level dyeing. Thus the use of a dyebath containing 5% sulphuric acid and 20% Glauber's salt on the weight of goods may be considered to be satisfactory for the application of chrome-complex dyes so far as levelling is concerned.

The addition of non-ionic level-dyeing agents does not cause any further improvement in levelling in such dyebaths except in one or two cases. The improvements obtained in the cases of Ultralan Orange RS and Ultralan Pink BNS, as shown in Table X, are not in themselves sufficient to warrant the use of such agents, although such improvements are valuable.

Several indications of the nature of the mechanism of complex formation between Lissapol N and dye are given by the results. The results in Table IX, obtained with the Ultralan dye bases, show that the chelated chromium in the dye is not necessarily

involved in the complex formation. The solubility in toluene of the Lissapol N–dye complex suggests that Lissapol N attaches itself to the dye in such a way as to diminish the hydrophilic character of the latter. It is probable, therefore, that complex formation involves the acid groups in the dye molecule.

The reactions of the Ultralan bases show that complex formation with Lissapol N is not restricted to chrome-complex dyes. The rôle of the acid group in complex formation is not clear, since there is little possibility of any ionic reaction with the non-ionic agent. The most probable explanation from consideration of the results is that molecules of water associated with the dye in solution are involved. It is known that Lissapol N and other non-ionic agents in solution dehydrate to some extent as the temperature is raised, and it has been suggested by Valkó [4] that the increased aggregation of Palatine Fast Blue GGN (IG) with increasing temperature is due to dehydration. Thus it is likely that complex formation takes place by replacement by the agent of water associated with the dye. In fact, the dehydration of the dye may well be assisted by the agent.

Such a reaction will result in the replacement of water associated with the dye by a dehydrated non-ionic body. Thus the hydrophilic properties of the dye will be lessened, and some solubility in non-polar solvents developed. This theory is substantiated by the results of the partition experiments carried out in the presence of toluene.

An alternative explanation of complex formation is that the dye is soluble in the agent and that solution effects alone have been observed. This is, however, contradicted by the results in Tables VII and VIII. Both sodium acetate and lithium thiocyanate are shown to increase complex formation between Lissapol N and Ultralan Dark Green BS. However, they have contrary effects on the solubility of Lissapol N in water, sodium acetate decreasing it and lithium thiocyanate increasing it. Their effects on the solubility of the dye–Lissapol N complex would be expected to be in line with their effects on the solubility of Lissapol N itself. Moreover, the specific action of sodium acetate on the complex formation of Ultralan Dark Green BS cannot be explained purely on the basis of solubility.

It is almost certain that complex formation takes place between the dye and the Lissapol N with an increase in particle size and in rate of surface absorption of dye by the fibre. It is in this sense that Valkó's theory of competition for the dye between fibre and agent [4] is correct. The dye will diffuse into the fibre from an adsorbed layer of the complex. The adsorption of the complex by the fibre, being purely a surface phenomenon, will bear little relation to the damage sustained by the fibre. The rate of adsorption of the dye from the adsorbed complex by this fibre will increase with increasing damage, but owing to the fact that dyeing does not take place by free adsorption from the dye liquor, the advantage of damaged over undamaged wool is considerably reduced, which minimises skittery dyeing.

It is well known, of course, that dyes which aggregate in solution, e.g. acid milling dyes, tend to give skittery results. There is, however, no contradiction between this fact and the theory that non-ionic agents prevent or reduce skitteriness by the formation of a complex with chrome-complex dyes, with a resultant increase in particle size.

In the case of acid milling dyes the aggregate itself has all the characteristics of a dye molecule in that it possesses affinity for the fibre and is able to diffuse into the fibre providing it does not exceed a certain maximum size. The aggregation of the milling dye tends to accentuate skitteriness in that the larger pore size of certain damaged fibres promotes more rapid diffusion of the dye into these fibres. Moreover, the lack of levelling properties with acid milling dyes applied by acid or weakly acid processes prohibits the removal of skitteriness by subsequent levelling in the boiling dyebath.

On the other hand, the aggregate of Lissapol N with chrome-complex dye, it is postulated, cannot diffuse into the fibre except to a very small extent, i.e. only in the most damaged fibres. Diffusion of chrome-complex dye into the fibre can take place only by breakdown of the complex which is adsorbed on the fibre surface. Thus it may be said that competition takes place between the fibre and the agent for the chrome-complex dye. The mechanism of such a process has recently been described by Millson and Turl [5], who have given actual photographs of it occurring with cationic agents. It may be concluded that, in the case of chrome-complex dyes and non-ionic agents, the more complex the aggregate that is formed and the larger the particle size the more likely it is that skittery dyeing will be prevented.

That this picture of the dyeing process corresponds with the experimental observations is shown by the results in Table XIII, compiled from Tables III and XI.

TABLE XIII

Relation between Complex Formation and Improvement in Skittery Dyeing of the Ultralan Dyes with Lissapol N

	Complex Formation with Lissapol N (%)	Reduction due to Lissapol N in Time to achieve Levelness (min.)
Ultralan—		
Orange RS	94	30
Red RS	89	30
Yellow RS	84	35
Orange GS	78	25
Blue 2GS	72	10
Pink BNS	36	15
Dark Green BS ...	31	15
Bordeaux RS ...	19	20
Bordeaux BS ...	5	0
Red BS	4	0
Violet 5RS	0	5

There are certain slight discrepancies in the results, but these are most probably due to the qualitative nature of the skittery-dyeing test. A more accurate test was not required for the

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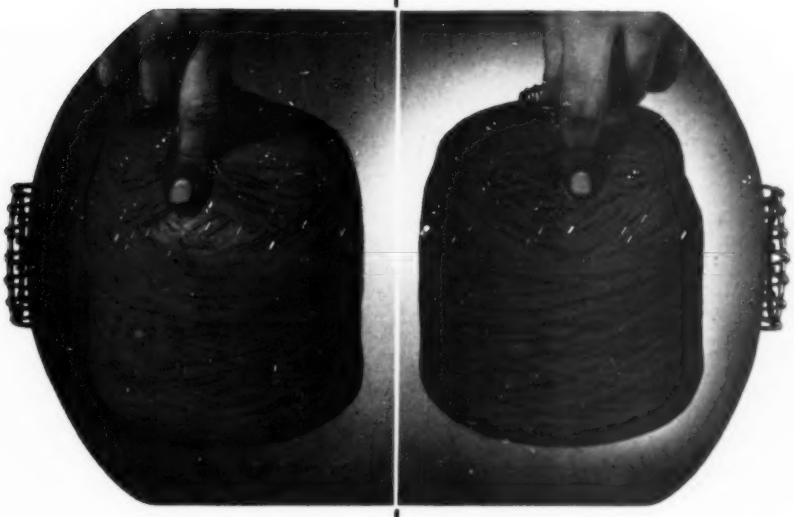

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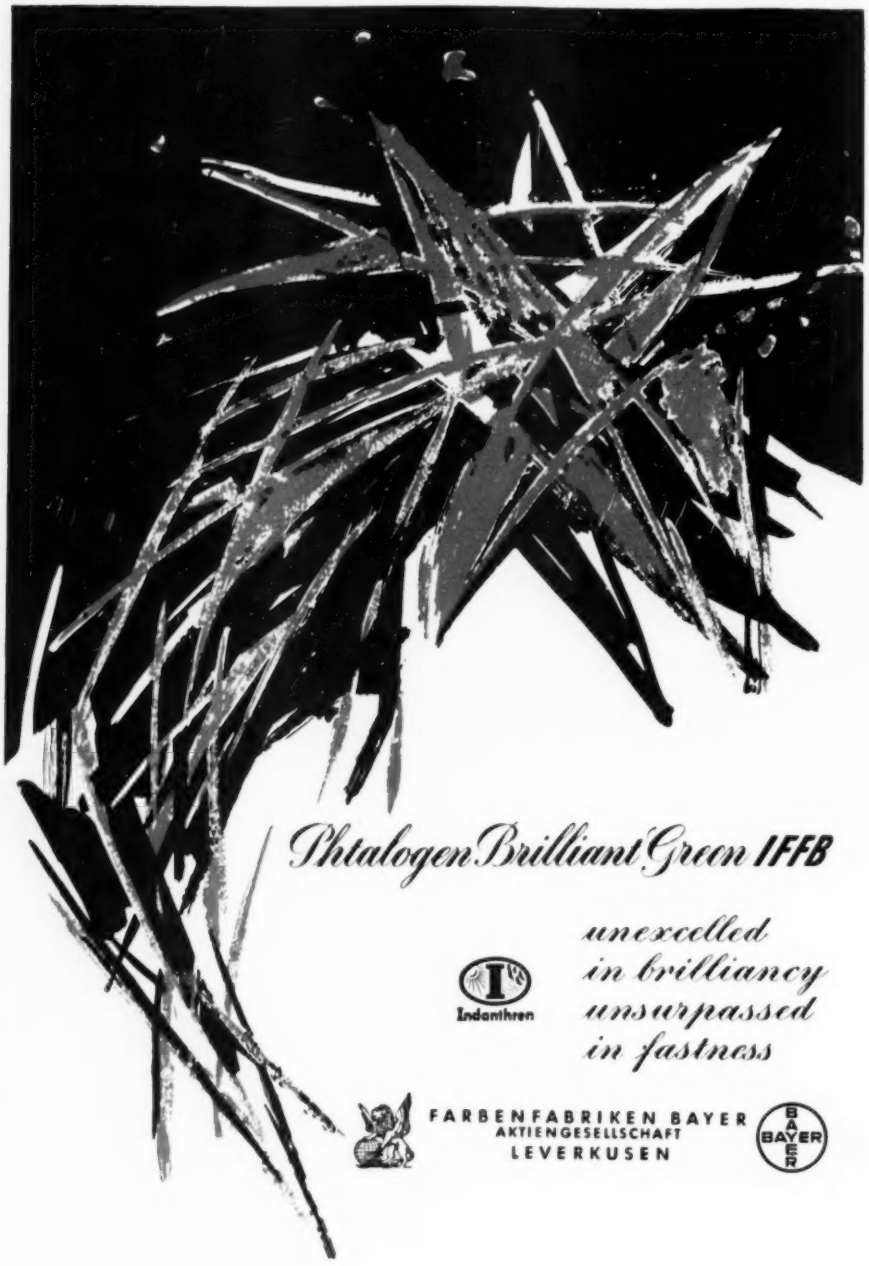
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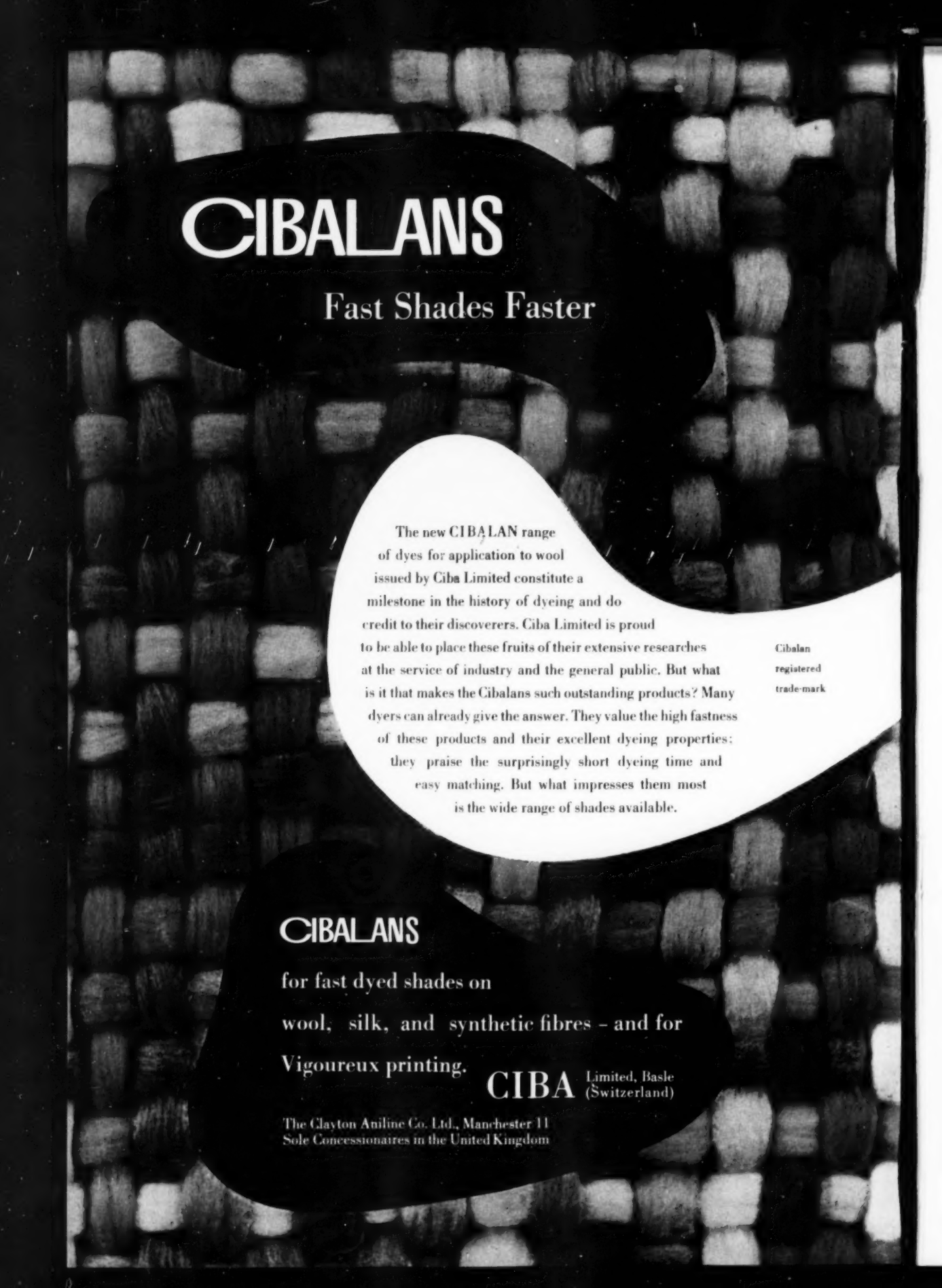
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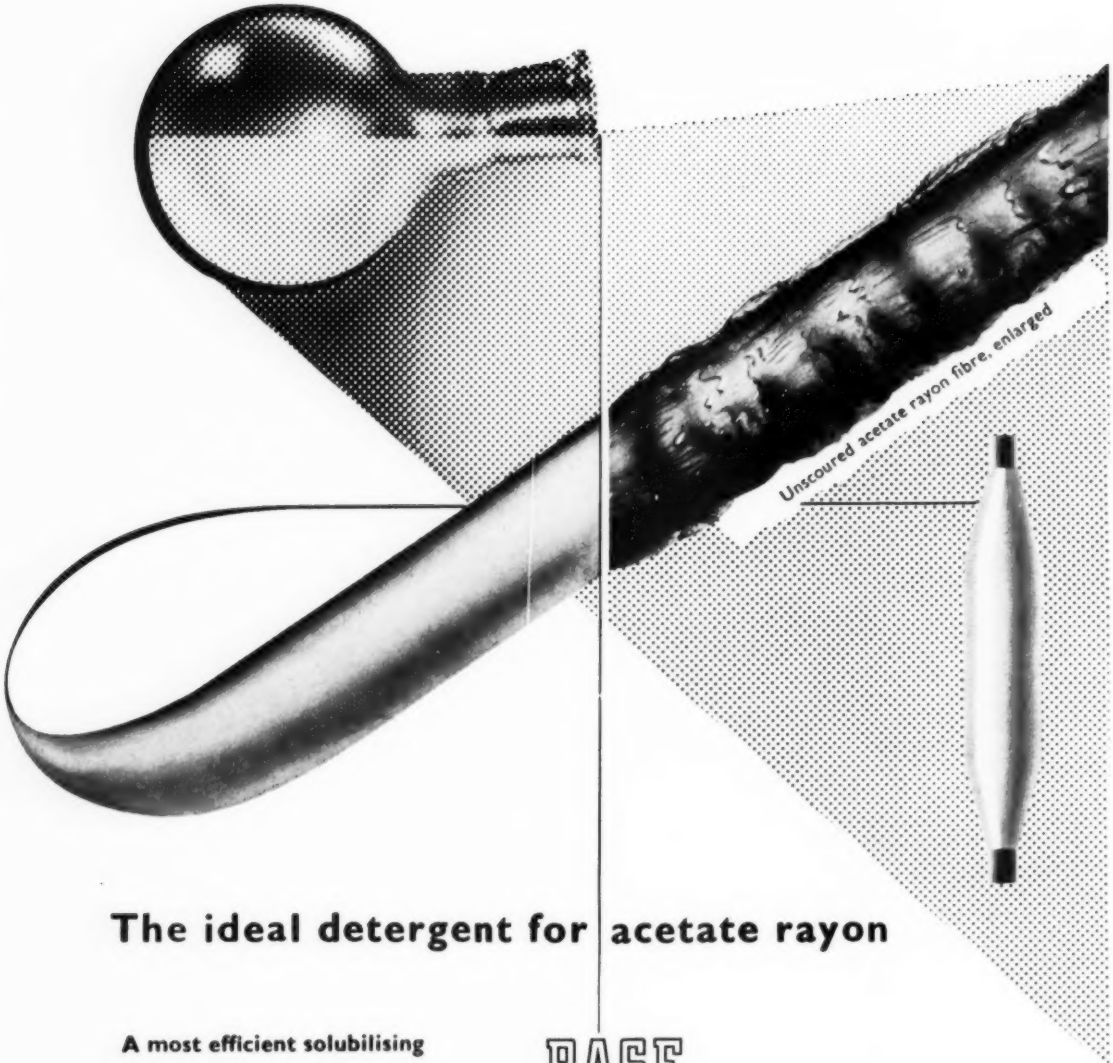

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purpose of this work, since a quantitative relationship between skittery dyeing and complex formation was not being sought. The results of bulk dyeing trials indicate that, in any case, the use of chlorinated and normal wool as a standard of skittery dyeing considerably exaggerates that phenomenon, and that the results are basically correct so far as practical dyeing is concerned.

For the practical dyer these results indicate the extent to which level-dyeing agents of the non-ionic type may be expected to give level results with chrome-complex dyes. The use of these agents does not replace the loss of levelling power sustained by the dye with reduction of acid in the dyebath, which decreases the margin of error for the dyer and necessitates greater reliance on such environmental factors as the type of machine used, the efficiency of circulation, and the temperature distribution. It may not be possible, therefore, for all dyers with all machines to reduce the quantity of acid employed even with the use of non-ionic level-dyeing agents. The use of such agents will, however, enable the dyer to achieve improvement, and it is certain that in the vast majority of cases successful results can be obtained providing that the loss of levelling power of the dye is minimised by the use of 5% sulphuric acid (98%) and 20% Glauber's salt. It is clear also that Lissapol N offers distinct advantages over agents of the Dispersol A type in that, owing to its relatively low solubility at the boil, it does not cause any frothing or flotation in the dyebath. This property of Lissapol N appears to be the basis of its greater effectiveness, in so far as it may be assumed to form complexes of greater particle sizes than do other agents and at the same time to possess low surface-active properties in the boiling dyebath. The use of 1–2% Lissapol N on the weight of goods may therefore be considered as of more value than the additions previously recommended (e.g. 4% Dispersol A).

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Estimation of Free Aldehyde Groups in Oxycelluloses

Most of the various methods suggested for the estimation of reducing groups in oxycelluloses are extensions of the methods used for the estimation of the same groups in simple sugars, e.g. glucose and maltose, and thence for the estimation of the sugars themselves. In none of these methods is there a stoichiometric relation between the standard oxidising agent consumed and the number of reducing groups present, for the principal oxidation is complicated by side reactions. It has been reported that from 1 to 5 atoms of oxygen are consumed for each reducing group present, according to the choice of oxidising agent and other experimental conditions [1–5]. Richardson, Higginbotham, and Farrow [5], using the copper number determination, found the relation to be 5 atoms of oxygen, corresponding to 10 atoms of copper transformed from the cupric to the cuprous state, for each reducing group in maltose. In these determinations, the normal procedure was modified in order to avoid the errors introduced by the loss of colloidally dispersed cuprous hydroxide in the filtrate when the alkaline copper reagent is removed. The value of 10 for the copper equivalent of the aldehyde group has been used by Richardson *et al.* [5] in their work on starches and by Nabar, Scholefield, and Turner [6] in studies of the oxycelluloses which result when cotton cellulose is oxidised with sodium hypochlorite in the presence of certain reduced vat dyes.

More recently, Harris and co-workers [7] have suggested that buffered sodium hypoiodite solution should be used to estimate the aldehyde groups present in periodate oxycelluloses. Pacsu [8] has criticised this method adversely because (i) the hypoiodite reagent is unstable and (ii) periodate oxycelluloses are themselves unstable, even though the buffer employed is only weakly alkaline. Some experiments carried out in this laboratory have shown that, in the estimation of glucose, the oxygen consumed is not stoichiometrically related to the aldehyde groups present, even after 24 hr. Hiller and Pacsu [9] have suggested the use of acid permanganate as a reagent, and have described a method which they claim to be specific for the determination of aldehyde end-groups in cellulose and in hydrolysed celluloses. Methods based on the use of hydroxylamine hydrochloride [10] and of methylhydroxylamine hydrochloride [11] have also been described.

After a survey of the methods available, it was considered that there was scope for a further examination of the problem of the estimation of aldehydic groups in oxycelluloses. These groups may be estimated (*a*) by a method in which they are oxidised and the consumption of oxidising agent is measured (the principle adopted in almost all the foregoing methods) or (*b*) by quantitative oxidation of each –CHO group to –COOH followed by a determination of the increase in –COOH content of the treated oxycellulose. For the methods included in (*b*) above, the following properties are

TABLE I

Effects of Treatment with Chlorous Acid on Carboxyl Content and Copper Content of Oxycelluloses

Sample No.	COOH Content (I — m-equiv./100 g.) Before (*a*)	After (*b*)	Copper Number (II) Before (*a*)	After (*b*)	Increase in COOH (III = I*b* − I*a*)	Decrease in Cu No. (IV = II*a* − II*b*)	Ratio $\left(V = \frac{III}{IV}\right)$	Copper Equiv. $\left(VI = \frac{\text{Cu atoms}}{CHO}\right)$
PERIODIC-ACID OXYCELLULOSES								
1	1·0	6·6	2·61	0·34	5·6	2·27	2·47	6·38
2	1·0	10·05	4·08	0·54	9·05	3·54	2·56	6·16
3	1·2	16·45	6·54	0·85	15·25	5·69	2·68	5·87
4	1·5	21·3	8·71	1·00	19·8	7·71	2·57	6·13
5	2·29	46·8	19·0	1·53	44·5	17·47	2·55	6·18
6	2·66	25·3	10·2	1·02	22·6	9·18	2·46	6·39
						Mean ...	2·55	6·19
DICHROMATE–OXALIC-ACID OXYCELLULOSES								
7	7·87	25·6	20·2	2·54	17·73	17·66	1·00	15·7
8	4·92	15·3	11·73	1·53	10·38	10·20	1·02	15·5
9	0·72	2·47	1·99	0·19	1·75	1·80	0·97	16·2
10	1·03	4·23	3·54	0·33	3·20	3·21	1·00	15·8
11	1·34	5·88	5·25	0·49	4·54	4·76	0·95	16·5
12	1·76	7·74	6·39	0·57	5·98	5·82	1·03	15·3
						Mean ...	1·00	15·83

desirable in the reagent selected to perform the preliminary oxidation of –CHO groups— (i) it should be acidic in order to avoid the secondary hydrolysis by alkali to which periodate and dichromate oxycelluloses are sensitive; and (ii) the acid should not cause hydrolysis of the oxycellulose during treatment. According to Jeanes and Isbell [12], aldoses are transformed quantitatively to aldonic acids by chlorous acid (acidified sodium chlorite). The action of this reagent in oxidising the –CHO groups of periodate oxycelluloses to –COOH has been investigated by Harris *et al.* [7], Davidson and Nevell [13], Pinte and Rochas [14], and Miller [15].

In Table I are given the results of experiments with (i) celluloses oxidised with periodic acid [13] and (ii) celluloses oxidised with potassium dichromate and oxalic acid [16]. The reducing power and –COOH content of each product were determined, first before and then after treatment with 0·1 M. sodium chlorite in 0·5 M. phosphoric acid at room temperature for 24 hr. Carboxyl contents have been determined by an iodimetric method [17] and reducing power by Heyes' modification [18] of the Braidy copper number method. In this method, the weight of the sample of modified cellulose required is normally 0·25 g. and the volume of the alkaline copper reagent 10 ml. for each determination. Because some of the oxycelluloses had a high reducing power, these proportions were changed to 0·125 g. and 15 ml. respectively for all samples except No. 5–8 (Table I), where they were 0·1 g. and 100 ml. To allow for the slight solubility of the liberated cuprous hydroxide in the alkaline reagent, saturation of the reagent with the hydroxide was ensured by the addition of a small known proportion of glucose along with the weighed sample of oxycellulose [5]. The effect of this addition was determined in control experiments.

From Table I it is seen that the value of V—

$$\frac{\text{Rise in carboxyl content after chlorite oxidation}}{\text{Fall in copper number after chlorite oxidation}}$$

is more or less constant for periodate oxycelluloses and again for dichromate oxycelluloses, but is different between one type and the other. In the chlorite oxidation, one –COOH group has been obtained from each –CHO group originally present in the oxycellulose, so that from ratio V it is possible to calculate the copper equivalent, i.e. the number of atoms of cupric copper reduced by one –CHO group in the copper number determination. This is given as value VI in Table I, and it is seen to be approx. 6 for periodate oxycelluloses and to be near 16 for oxycelluloses produced by the action of dichromate and oxalic acid.

It has been established that, when cellulose is oxidised with periodic acid, oxidation takes place, and aldehyde groups are produced, almost entirely at the 2 and 3 positions in the anhydroglucopyranose unit, one criterion of this being the rapid fall in tensile strength and the accompanying rise in fluidity when the oxycellulose is treated with dilute alkalis. In the dichromate–oxalic acid oxycelluloses, while the tensile strength relative to the degree of oxidation is high, fluidity is relatively higher and alkali sensitivity relatively lower than with periodate oxycelluloses. These observations lead us to believe that oxidation has produced aldehyde groups largely in the 6 position of the anhydroglucose unit. It will further be seen that the copper equivalents for two different kinds of reducing oxycellulose are different from the value given by Richardson *et al.* for glucose and maltose [5]. Thus there is evidence that, during the copper number determination, the proportion of oxygen taken up from the reagent (and therefore the proportion of copper reduced) by one reducing group in the oxycellulose can vary very markedly according to the method of preparation of the oxycellulose, and that this may be due to the position of the reducing groups in the affected unit.

A standard treatment of an oxycellulose with chlorous acid, together with determinations of copper number and carboxyl content before and after the treatment, thus promises to be of value not only in determining the proportion of aldehyde

groups but also in fixing their position in the original anhydroglucose unit.

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[14] Pinte and Rochas, *Bull. Inst. Text. France*, (21), 9 (1950).
[15] Miller, *TAPPI*, **34**, 171 (1951).
[16] Clibbens and Ridge, *J. Textile Inst.*, **18**, T 141 (1927).
[17] Nabar and Padmanabhan, *Proc. Indian Acad. Sci.*, **31**, 370 (1950).
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Colour Changes induced in Vat Dyeings by Organic Solvents

On some occasions in the manufacture of articles of wear, dyed fabrics are subjected to the influence of heat and of organic solvents under pressure. Since many organic solvents are capable of either dissolving or dispersing organic colouring matters, colour changes are sometimes observed which resemble those discussed earlier [1].

It was noticed that any colour change of vat-dyed fabrics was generally similar to that occurring in the transition of the dye from the amorphous to the crystalline state, but that on some occasions the colour change was in the reverse direction. It was also noticed that the former change usually took place with darker shades, whilst the latter occurred with lighter shades. This reversal of colour change was particularly conspicuous with dyeings of Soledon Blue 2RCS (ICI).

In order to investigate this phenomenon, dyeings of different depths of Soledon Blue 2RCS—using 0·15, 1·5, and 15 g. dye per litre—were prepared. The dyeings were well soaped, so that the true shade was as fully developed as was practically possible, and were then treated under heat and pressure with Soltex TDX (British Industrial Solvents Ltd.).

It was observed that the 0·15-g./l. dyeing became markedly greener. The 1·5-g./l. dyeing also became greener, but to a very much smaller degree, whereas the 15-g./l. dyeing became redder.

The original colour of the two lighter dyeings could be partly restored by the usual soaping treatment, but the colour change of the darker dyeing was permanent.

The behaviour of vat dyes under the conditions outlined above would be consistent with the conclusions arrived at in the previous papers [1]. Further crystallisation would appear to take place in the case of the darker dyeings, the mechanism being in principle the same as that obtaining during soaping, viz. preliminary (molecular?) dispersion of the dye by the solvent, with consequent ability to crystallise further under the conditions of treatment. In the case of the lighter dyeings, dispersion alone would seem to take place, there being insufficient dye present to allow for renewed association of the dye molecules to crystalline aggregates under those conditions. On subsequent soaping, conditions for association would appear to be more favourable, and some crystallisation would seem to occur, with consequent partial restoration of the original colour.

In view of statements made in a recent paper [2] on this subject, it might be mentioned that the crystallisation which is thought to underlie the colour change need not necessarily lead to the formation of microscopic crystals, but that rearrangement of the dye aggregates in the form of an orderly crystal lattice is quite sufficient to effect the colour change.

* * *

Thanks are due to Imperial Chemical Industries Ltd. for the preparation of the dyeings, and to the Directors of Trubenised (Gt. Britain) Ltd. for permission to publish this letter.

E. Kornreich

39 Park Street
London W.1

6th May 1953

[1] Kornreich, E., J.S.D.C., **58**, 177 (1942); **62**, 318 (1946).
[2] Wegmann, J., *Textil-Rund.*, **8**, 4 (Jan.), 97 (March), 157 (April 1953).

ERRATUM

The Effects of the Soaping Aftertreatment on Vat Dyeings. H. H. Sumner, T. Vickerstaff, and E. Waters (J.S.D.C., **69**, 191 (June 1953))—The word **Fortisan** is the registered trade mark of British Celanese Ltd. and is used to identify strong yarn produced by the stretching and saponification of cellulose acetate. The Editor regrets the error in ascribing this trade name to another firm.

Notes

Proceedings of the Council

At a meeting of the Council held at the offices of the Society, 19 Piccadilly, Bradford, on 15th July 1953, the proceedings included the following items of interest—

W.I.R.A.— It was resolved that the deep gratitude of Council be conveyed to the Council and the Director of Research of the Wool Industries Research Association for their generosity in allowing Mr. John Barritt to devote so much of his time to the affairs of the Society during his period of office as Honorary Secretary.

Mercer Lecture Committee— The resignation of Mr. G. S. J. White, due to pressure of other business, was accepted with regret, and gratitude was expressed for his past services.

Mr. J. Boulton— Mr. Boulton was congratulated upon his appointment as Honorary Secretary of the Textile Institute. His resignation from the Committee on the Dyeing Affinity of Regenerated Cellulose and from the Light Fastness Subcommittee, due to his many other commitments, was accepted with regret, and he was warmly thanked for his past services as Chairman of both Committees. Mr. Boulton said that members of his staff would continue to take an active part in the work of these committees.

B.S.I. Silk Industry Committee— Mr. G. F. Wood was invited to represent the Society on this committee.

Finance Committee— It was resolved that the Chairman of the Publications Committee should be *ex officio* a member of the Finance Committee.

Symposium Dinner— It was reported that Mr. R. M. L. Lee (Chairman of the Calico Printers' Association Ltd.) had accepted an invitation to be the Society's chief guest at the dinner to be held on the occasion of the Symposium on Textile Printing.

Golf Trophies— The President (Mr. F. L. Goodall) and Mr. R. J. Hannay were warmly thanked for their generosity in offering to present a challenge trophy and the second prize for award at the golf competition to be held in connection with the Symposium. It was intended that the trophy would be competed for annually by members of the Society.

Membership— Ten applications for ordinary membership and one for junior membership were approved.

Meetings of Council and Committees July

Council— 15th
Publications— 21st
Colour Index Editorial Panel— 22nd
Joint Conference— 22nd

The Association of British Chemical Manufacturers

The telephone numbers of the A.B.C.M. offices at 166 Piccadiily, London W.1, have been altered to HYDe Park 4126–7 and 1557–8. The change affects also several affiliated associations, including the British Colour Makers Association.

Production and Sales of Dyes during 1952 in the U.S.A.

The U.S.A. Tariff Commission reports that the total production of dyes in the U.S.A. in 1952 was 145 million lb., a decrease of 23% on the 187 million lb. produced in 1951. Sales in 1952 were 149 million lb. valued at $171 million compared with 166 million lb. valued at $177 million in 1951, a decrease of 7% in weight and 3% in value. The average price was $1.15 per lb. in 1952 compared with $1.10 in 1951.

Vat dyes formed 39% of the total production, and direct cotton dyes 18%. Azo dyes formed 34% of the total production, anthraquinonoid vat dyes 25%, indigoid and thioindigoid 14%, and sulphur dyes 13%. The weight of azo dyes produced in 1952 decreased by 27% compared with 1951, that of anthraquinonoid vat dyes by 13%, that of indigoid and thioindigoid by 1%, and that of sulphur dyes by 12%. Production of azoic dyes and components decreased by 7·5%, being 7 million lb. in 1952 compared with 7·5 million lb. in 1951. Sales of azoic dyes in 1952 were 6·7 million lb. of value $13·1 million, an increase of 10% on 1951. Production of azoic compositions decreased slightly, being 1·3 million lb. in 1952 compared with 1·4 million lb. in 1951, whereas that of diazo components increased by 81%, being 2 million lb. in 1952 and only 1·1 million lb. in 1951. C O C

OBITUARY NOTICE

George Edward Holden

The recent death of George Edward Holden, C.B.E., M.Sc., F.R.I.C., marked the passing of one who gave a lifetime of service to the Society. A contemporary of the late Edmund Knecht, he was a most active member of the Manchester Section Committee of those earlier days. His term of office as Chairman was outstanding, not only for the high standard of lectures, but for his efforts to introduce a better social atmosphere amongst the members, thereby welding them into a compact body, rather than a collection of individuals. His genius for friendship endeared him to all with whom he came into contact, making each one feel that his personal friendship really mattered. It was significant that he was known as "George" to so many people.

President of the Society from 1948 to 1950, his Chairmanship of the Council was marked by great tact and courtesy, which went a good way in smoothing out difficulties and differences of opinion, making real progress possible. A full-page portrait appeared in the March 1950 issue of the *Journal*.

In 1951 the Council recorded its appreciation of his outstanding services to the Society and to the dye-making and dye-using industries by making him an Honorary Member of the Society.

Outside the Society his talents were recognised by many high appointments— Dyestuff Controller from 1946 to 1951, Technical Adviser of the Dyestuffs Import Licensing Committee, a member of the Dyestuffs Industry Development Committee, then a special Technical Adviser of the Dyestuff Control Committee, as well as Prime Warden of the Worshipful Company of Dyers for a term. All these offices testified to his profound knowledge of dyes and their uses, a fact recognised by the Board of Trade by the award, first of the M.B.E., and later of the C.B.E.

He was Chairman and Managing Director of English Velvets Ltd. until his retirement as Managing Director in 1949 and as Chairman in 1951, and his connections with the velvet trade led to appointments on many trade association committees, where he was held in the highest esteem.

How far all these activities contributed to the unfortunate breakdown in health during his last few years is a matter of conjecture, but it is a great pity that a life of such intense activity should not have had a longer and happier retirement. His services to science and industry deserve high praise indeed.

G. M. WILLIAMS

New Books and Publications

Detergents

What they are and what they do

By Donald Price. Pp. 159. New York: Chemical Publishing Co. Inc. 1952. Price, $4.00.

In a foreword the author states that the aim of his book is to tell the story of how detergents developed and of what they do, in a language that the non-technical reader can understand. It is pertinent to discover with what success the author has been able to achieve this aim.

The book starts by explaining the molecular structure of soaps and synthetic detergents, and goes on to trace the history of soap and the development of synthetic detergents. No attempt is made to distinguish between sulphonation and sulphation, and it is not now correct to say that a disadvantage of non-ionic detergents is that they must be used in the form of aqueous solutions, as in suitable admixture spray- or drum-drying may be effected. This is, in fact, pointed out in the last chapter.

The third chapter deals with the nature of dirt, and then explains some concepts of colloid chemistry, but does not too clearly relate these to detergency. The explanation of dirt removal would have been clarified by reference to Adam's observation of the "rolling-up" of oil when an oiled fibre is immersed in a detergent solution. It cannot be agreed that research on the action of detergents has been "relatively neglected". The statement that cotton is the most difficult fabric to wash clean needs some qualification. The chapter then goes on to discuss surface tension, foam, and pH. The statement that "foam has an important rôle in the removal of dirt" should certainly be amplified, especially in view of the preceding sentence that "some materials produce a great deal of foam in water without being detergents at all and there are some quite good detergents that give little or no foam". The statement that pH can be measured to several more decimal places than the first is also open to question, at least as far as ordinary pH meters are concerned. A serious omission is the absence of any reference to redeposition, which surely should be included in this chapter explaining the mechanism of detergents, and not restricted to the somewhat brief mention in connection with carboxymethyl cellulose in the chapter on household detergents. This latter chapter ends with the statement that cleaners based on the synthetics do have limitations, but no discussion of these limitations is given. Laundering is not dealt with in the chapter on industrial detergents, while the space given to wetting agents seems rather out of place in a book on detergents.

The chapter on testing includes also sections on the testing of wetting agents and emulsifying agents; the purpose of the surface tension measurement described is not explained. The concept of suspending power is also introduced in this chapter, but no method of measuring redeposition is described. It is not necessarily correct to say that one is obliged in detergency testing to use much heavier soils than are met with in practice, although this is most commonly done.

Throughout the book the term "soil" is often used for dirt, which, in a book intended for non-technical readers, may well lead to confusion.

One cannot escape the conclusion that some sections of the book will be difficult to understand unless the reader has some knowledge of elementary chemistry. The presentation is not always logical, and, as indicated in the more detailed comments which have been given, some misleading information is included. Nevertheless, there is no other small book available presenting information about detergents in as simple a form, although the price is high for such a book. No review of this book should fail to mention the entertaining drawings with which the chapters are headed.

R. E. WAGG

Manufacturers' Publications and Pattern Cards

The Society does not accept any responsibility with regard to the statements in the following notes. Any publication abstracted may be referred to by members of the Society on application to Dr. C. B. Stevens, Dyeing Department, Leeds University

Cassella Farbwerke Mainkur

AQUAMOLLIN BCS LIQUID—This is a new brand of the older water-softening agent, Aquamollin BC liquid (formerly Corrigon BC liquid). It is cheaper than the latter and is recommended as an addition where trouble is likely to occur owing to the presence of salts of calcium, magnesium, iron, copper, and manganese. It is also of interest for removing these metals from textiles, e.g. copper and manganese from goods to be rubberproofed, iron stains, and mineral khaki dyeings.

IMMEDIAL FAST YELLOW GWL, BROWN AL, OLIVE BROWN TL, KHAKI AL, GREEN GHL EXTRA—Dyeings are shown of these five new sulphur dyes in four depths on cotton and viscose rayon dyed direct and aftertreated with potassium dichromate–copper sulphate. Dyeings have good fastness to light and wet treatments, the fastness to washing at 100°C. being still further increased by aftertreatment with Solidogen FFL.

MAPRINTEN K and L—These auxiliary products are recommended as stabilising agents for addition to vat-dye printing pastes to improve the resistance of vat prints to storage prior to steaming. With most dyes, maximum stability is obtained when both products are incorporated in the paste.

Les Colorants de Tertre S.A.

TERTROXANE DYES ON WOOL CLOTH—This card contains dyeings in two depths of 36 Tertroxane (metal-complex) dyes and 18 mixture dyeings.

TERTROXANE DYES ON WOOL YARN—This card contains dyeings in two depths of the same range of dyes as in the previous card, together with 18 mixture dyeings.

DYES FOR WOOL—This card contains dyeings in two depths on yarn of 40 Tertracid and 24 Tertrochrome dyes.

DYES FOR COTTON—This card contains dyeings in two depths on yarn of 48 Tertrodirect, 40 Tertrodirect Fast, and 16 Tertrosulphur dyes.

Farbenfabriken Bayer

BENZAMIN RUBINE F3BD—This direct dye gives full magenta reds on cellulosic fibres when diazotised and developed with Developer AN. Crease-resist finishing with Kaurit KF or Cassurit MKF does not impair the fastness to light, and dyeings may be readily discharged to a good white if Type 8002 is used. Acetate rayon effects are only slightly stained if Type 8000 is used in conjunction with Developer AZ. This dye is also of interest for producing readily dischargeable dyeings on silk from a weakly acid bath. Some fastness figures for a diazotised and developed dyeing on cotton include—Light 4, washing at 40°C. 3–4, perspiration 4.

BENZO FAST COPPER BLACK RL and GL—These two direct cotton dyes give reddish and greenish blacks, respectively, on cellulosic materials when aftertreated on the fibre with either Benzo Fast Copper Salt or copper sulphate. Dyeings have very good fastness to light and good fastness to wet treatments. The RL brand is suitable also for coloured discharge printing. Fastness figures on cotton include—Light 7 (as a black), washing at 40°C. 4, perspiration 4–5.

PHTHALOGEN BRILLIANT BLUE IF3G IN PIECE DYEING—This card describes the application of this product to cellulosic cloth by a continuous padding process. The high fastness of dyeings to light and wet processing coupled with brightness of hue makes it particularly suitable for curtains and furnishing fabrics. Application involves the padding of the material in a solution of the dye (obtained with the assistance of Levasol P8) and the developing agent, Phthalogen CU (a copper salt plus an organic compound); the padded material is then dried at 70–80°C., and developed by heating at 140–145°C. for 2–8 min. followed by an aftertreatment at 60–100°C. in an acid solution to remove secondary products and then a final soaping.

SIRIUS SUPRA ORANGE 3GLD and 3RD—These two direct cotton dyes give yellowish and reddish oranges, respectively, of good fastness to light on cellulosic fibres. Fastness to wet treatments is considerably improved by aftertreating the dyeings with Levogen WW. A recommended application is in the production of dischargeable grounds using Type 8002 and neutral or alkaline conditions. Fastness figures on cotton include—

Sirius Supra Orange 3GLD: Light 6–7, washing at 40°C. 2 (aftertreated with Levogen WW, 4).

Sirius Supra Orange 3RD: Light 6, washing at 40°C. 2 (aftertreated with Levogen WW, 3).

SIRIUS SUPRA SCARLET BN—This direct cotton dye gives yellowish reds of good fastness to light on cellulosic fibres, and is suitable for use in circulating-liquor machines and for the continuous dyeing of cloth. Type 8002 is particularly suitable for discharge printing on cotton under either neutral or alkaline conditions. Very good tone-in-tone dyeings are obtained on cotton–viscose rayon mixtures, while acetate rayon is virtually unstained if Type 8000 is used. Fastness figures on cotton include—Light 5–6, washing at 40°C. 3, perspiration 3.

SIRIUS SUPRA YELLOW RDA—This direct cotton dye gives bright reddish yellows having good fastness to light on cellulosic fibres. Aftertreatment with Levogen WW increases the fastness to water and perspiration without affecting either the hue or the fastness to light of the dyeing. A particular field of application is the production of dyed grounds for subsequent discharging under neutral or alkaline conditions. Fastness figures on cotton include—Light 6, washing at 40°C. 3 (aftertreated with Levogen WW, 5).

Imperial Chemical Industries Ltd.

CALEDON PRINTING BROWN 4R—This homogeneous vat dye is recommended for printing all types of cellulosic material to give full red-browns characterised by very good fastness to light, severe washing, and piece bleaching. No appreciable change in hue occurs with increasing depth, there is no gross difference in hue on cotton and viscose rayon, and prints do not change colour in artificial light. It is suitable for use as an illuminating colour in discharge styles, and is not recommended for use as a ground shade for subsequent discharge printing. Fastness figures for prints on cotton include—Light 6–7, washing (repeated severe, 5 times at 100°C.) 4–5, hypochlorite (dry chemicking) 5.

CHLORAZOL DIAZO RED 4B—This direct cotton dye when diazotised and developed on the fibre with β-naphthol gives bluish reds of good fastness to repeated mild washing. It is recommended for dyeing all forms of cotton yarn and fabric, and may also be of interest on weighted and unweighted silk. Ground shades on cellulosic materials are dischargeable to a good white with acid or neutral Formosul, and also with alkaline Formosul in the case of cotton. Coloured discharges only are possible on silk. It is not of interest for direct printing. Fastness figures for a diazotised and developed dyeing on cotton include—Light 2, washing (repeated mild, 5 times at 40°C.) 3, perspiration 4–5.

DURINDONE PRINTING MAGENTA B and DURINDONE MAGENTA B—These homogeneous vat dyes are recommended for dyeing and printing cellulosic materials when bluish reds are required and brightness is of primary importance. Dyeings and prints are yellower on viscose rayon than on cotton. Dyeings are dischargeable with Formosul and Metabol WS, and the printing brand is suitable for use as an illuminating colour in discharge styles. Durindone Magenta B is of interest for producing full magenta dyeings on silk, but tendering of the fibre is likely to occur on exposure to light. Fastness figures for prints on cotton include—Light 4–5, washing (repeated severe, 5 times at 100°C.) 3–4, hypochlorite (dry chemicking) 5.

MONASTRAL FAST BLUE BS and LBS—These pigments have outstanding tinctorial power and brilliance and give colourings of exceptional fastness. The BS brand in reduced depth gives greenish blues, which become redder with increasing pigment content. It is suitable for letterpress and lithographic printing inks, particularly for three-colour

work, since it gives a close approximation to the theoretical blue. Other important uses include the colouring of distempers, water paints, wallpapers, and pastels. The LBS brand has been specially developed for inclusion in such compositions as paints, lacquers, and gravure inks, since, unlike Monastral Fast Blue BS, there is no dulling or loss of tinctorial strength such as may occur with the latter in the presence of organic solvents.

MONASTRAL FAST BLUE GS—This pigment is very similar to Monastral Fast Blue BS in properties and recommended uses. It is appreciably greener than the latter, and thus gives even brighter greens in mixtures with such yellows as Monolite Fast Yellow 10G. It is particularly suitable for letterpress printing inks, being very close to the four-colour blue of *B.S.* 1480:1949. Changes in hue and strength are likely to occur in contact with many organic solvents, and thus it is not recommended for use, without extended trial, in compositions containing solvents. Additional uses include book cloths, flooring compositions, wallpapers, and distempers.

POLYMON BLUE 3RS—This pigment for colouring plastics gives blues that are redder than can be obtained with Monastral Fast Blue BS or Blue 24480 but have the same fastness properties. Pastels are a little greener and duller than those obtained with Blue 18424. It has good heat stability, it is readily dispersible, and essentially non-bleeding in resins and plasticisers, and the colourings obtained even in pastels are comparable in fastness to light with those from Monastral Fast Blue BS.

SOLOCHROMATE FAST BORDEAUX BN—This chrome dye may be applied to wool by all three methods, but is particularly recommended for dyeing loose wool and slubbing by a single-bath process to give wine reds of very good fastness to light and wet treatments. It is of interest as the red component in mixtures, and to a limited extent for dyeing yarn and cloth. It is suitable for dyeing Ardil protein fibre and unweighted silk by the afterchrome and chrome mordant methods. Fastness figures on wool dyed by the chromate process include—Light 6–7, alkaline milling 3–4, washing (repeated mild, 5 times at 40°C.) 4.

SOLOCHROMATE FAST OLIVE BS—This chrome dye is particularly suitable for application to wool by a single-bath process, but may also be dyed on-chrome or afterchrome. The olive greens so obtained have very good fastness to light and wet treatments, and the dye is of particular interest as a component in the production of mode shades on loose wool and slubbing. It is suitable for dyeing nylon and silk by the afterchrome process, particularly when high wet fastness is required. Fastness figures on wool dyed by the afterchrome process include—Light 6–7, alkaline milling 4, potting 3.

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I—PLANT; MACHINERY; BUILDINGS

PATENTS

Continuous Manufacture of Artificial Threads. N.V. Onderzoekingsinstituut Research. *BP* 691,204

Improvements in the passing of continuously produced sheets of viscose rayon threads through an aftertreatment bath, wave motion in the liquor being prevented by filling the trough beneath the sheet of threads with material resistant to the liquid and of such shape that liquid flow readily takes place. Thus glass balls of diameter 5–20 mm. are put into the trough to within a few mm. of the bottom of the sheet of threads. C. O. C.

Continuous-filament Drier. Phrix-Werke. *BP* 692,133

Continuous filaments are dried in an unstretched condition by passing in loose loops through a drying zone on to a horizontal conveyor, the filaments being guided by a current of air. W. G. C.

Compressive Shrinking of Webs. Cluett, Peabody & Co. *USP* 2,615,230

In machines where reversal of the curvature of a travelling blanket is used to cause compressive shrinkage of a web, the intake roll is mounted so as to reduce its tendency to deflect from its intended position under the influence of the blanket. This enables smaller-diameter and hence lighter rolls to be used than would be otherwise possible, and so machines can be made which will satisfactorily treat very wide fabrics. C. O. C.

Felting Machine. Failsworth Hats. *BP* 691,270

In machines where several rollers are arranged with parallel axes in two horizontal banks, the upper and lower roller in each bank being pressed towards one another by springs, more efficient felting action is obtained if all the rollers have surfaces corrugated by longitudinal flutes and lands. C. O. C.

Hat-finishing Machine. W. C. Griffing. *USP* 2,615,599

A machine which will finish hat brims with welted edges, which is superior to the ordinary pouncing machine in its removal of surface hairs and in its ability to lay fine fur down smoothly and evenly without rubbing dirt and particles removed from the hat into the material of the hat, and which gives a more uniform finish colour to the hat. C. O. C.

Pouncing Machine with Heated Grease Pad. Doran Brothers. *USP* 2,615,600

A simple and double heated grease pad which applies sufficient grease to even and darken the colour of the hat and to retain properly the powder after it has been used. C. O. C.

Drums, Vats, etc. for Wet Processing of Leather. Cyril Norris & Son. *BP* 692,207

A door in the side of the container slides between parallel guides, shaped to follow the contour of the side of the container. The guides are fastened one on each side of the opening, a flexible inflatable tube being placed in an outwardly directed channel provided around the outer rim of the opening and arranged, on inflation when the door is closed, to bear between the channel and the marginal edge of the inner door surface, thus forming a liquid-tight seal for the opening. C. O. C.

Drum-type Leather-working Machine. Svit. *BP* 691,895

In a leather-working machine where the leather is supported by a drum, the cutter roller is applied to the leather on the drum by hydraulic apparatus controlled by valve gear connected to an operator-controlled manipulating rod. The valve gear is operated by turning this rod about its axis. C. O. C.

Cropping (X p. 311).

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Synthetic Detergents up to Date—II. J. W. McCutcheon. *Soap Sanit. Chemicals*, **28**, (7), 48–57; (8), 52–63; (9), 52–61; (10), 50–61 (1952): *Chem. Abs.*, **47**, 4634 (10 May 1953).

Statistics relating to soap *versus* synthetic detergents, a glossary of terms, and a brief review of technical advances are accompanied by a table giving information on 1005 proprietary detergents (name, manufacturer, class, formula, main uses, form, strength, type, and brief remarks). C. O. C.

Direct Synthesis of Alkyl- and Aryl-halogenosilanes. A. V. Topchiev and N. S. Nametkin. *J. Gen. Chem. U.S.S.R.*, **23**, 76–83 (Jan. 1953).

An examination is made of the products of the reaction under various conditions of silicon with methyl bromide and with bromobenzene in presence of copper. $(CH_3)_2SiBr_2$, CH_3SiBr_3, $C_6H_5SiBr_3$, and $(C_6H_5)_2SiBr_2$ are isolated in the pure state. A. E. S.

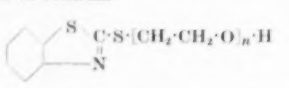
PATENTS

Alkarylsulphonate Detergents. Atlantic Refining Co. *USP* 2,615,847

Products of improved colour, giving stable aqueous solutions, are obtained by adding a little xylene to alkylated aromatic hydrocarbons before sulphonating them. C. O. C.

Wetting and Detergent Agents. Monsanto. *BP* 692,414

Compounds of formula—



(n = 5–31) are wetting agents and detergents which are unaffected by hard water. C. O. C.

Composition for inhibiting Precipitation of Multivalent Metals in Caustic Alkaline Solutions. F. C. Bersworth. *BP* 692,449

An alkali-metal alkoxide of triethanolamine is incorporated in caustic alkali in sufficient quantity to react completely with any future iron impurity to form a soluble iron salt (viz. 1 mol. of triethanolamine per 2 Fe). Excess of water is removed, and to the dry NaOH–alkoxide mixture is added a small amount, e.g. 2–3%, as a 20% soln., of a tetra(alkali-metal) ethylenediaminetetra-acetate, which renders soluble any water-hardening constituents. The final mixture contains e.g. approx. 5 lb. of alkoxide and 2–3 lb. of the tetrasodium salt per 100 lb. of NaOH, and may be dissolved in commercial waters containing 5 p.p.m. Fe and of low to medium hardness without any precipitation, even on boiling for a long time, provided the pH remains > 8. J. W. B.

Finish for Yarns for Tyres, etc. DuP. *BP* 692,384

Good cord strength is obtained without sacrifice of bond strength by treating the yarn with a mixture of amine soaps of higher (C_{10}–C_{18}) saturated and unsaturated aliphatic acids, a phenol–aldehyde resin, and a butadiene copolymer latex, the ratio of resin to copolymer being 1 : 9–1 and that of butadiene to the other constituents of the copolymer latex being 1–40 : 1. C. O. C.

Quaternary Ammonium Mothproofing Agents. Gy. *BP* 692,332

Compounds of formula—

$$(CF_3)_m\left[(A^1\cdot NH\cdot CO\cdot CHR\cdot N(CH_3)_2\cdot Z)_nA^2\right]X$$

(A^1 and A^2 = residues of the benzene or naphthalene series containing no salt-forming groups; R = H, CH_3, or C_2H_5; X = anion; Z = bivalent aliphatic bridging member attached to the quaternary N atom by a C atom; m and n = same or different 1 or 2) are very effective mothproofing agents, and in very dilute neutral or weakly acid aqueous solutions have very good affinity for wool. The monoquaternary compounds, i.e. those in which n = 1, are rather more active than the corresponding diquaternary ammonium salts. Those in which A^1 and A^2 are radicals of the benzene series are preferable to those containing radicals of the naphthalene series; and those in which n = 1, Z = $CH_2\cdot CO\cdot NH$, and A^1 and A^2 are both substituted by CF_3 groups have excellent activity against moth grubs and very good fastness to washing. C. O. C.

***N*-Acylated Sulphonamides— Textile Assistants and Dye Intermediates.** Basf. *BP* 692,651

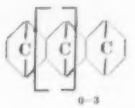
N-Acylated sulphonamides are readily obtained by heating carboxylic acids with sulphonyl *iso*cyanates—

$$R^1\cdot COOH + OCN\cdot SO_2\cdot R^2 \rightarrow R^1\cdot CO\cdot NH\cdot SO_2\cdot R^2 + CO_2$$

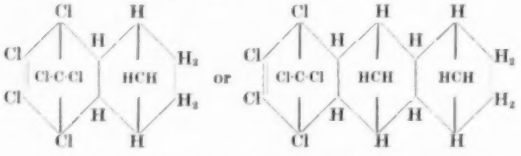
They are soluble in aq. bicarbonates or caustic alkalis, and may be used as textile assistants or dye intermediates. C. O. C.

Diels–Alder Condensation Products— Insecticides. Arvey Corpn. *BP* 692,545–7

Compounds of basic carbon atom skeleton—



in which one terminal five-membered ring contains a double bond in the unfused 2C bridge and bears only halogen atoms, the other terminal ring containing two univalent components attached to each of the two C atoms of the bridge, e.g.—



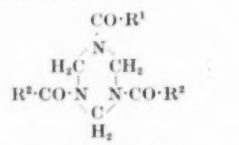
are highly active insecticides, unaffected by dilute alkalis. C. O. C.

Prevention of Rapid Gelation in Acidic, Aqueous, Colloidal Solutions of Unalkylated and Alkylated Melamine–Formaldehyde Condensates. American Cyanamid Co. *BP* 691,053

Aqueous solutions (12–40%) of the condensates are stabilised by adding urea and/or thiourea in excess of that necessary to combine with any uncombined formaldehyde present. C. O. C.

Polymers of Acryloyltriazine Aliphatic Amine Reaction Products. Sun Chemical Corpn. *USP* 2,615,882

Polymers of compounds of formula—



(R^1 = CA:CH_2; A = H, Hal, or Alk; R^2 = CA:CH_2 or addition products of CA:CH_2) are resinous materials of use for coating cloth, paper, etc. either alone or in conjunction with drying oils. C. O. C.

Solvents for Linear Polyamides. Polymer Corpn. *BP* 691,114

Synthetic linear polyamides soluble in phenol but insoluble in methyl alcohol at or below the boil are mixed with methyl alcohol and heated under pressure until dissolved. The solutions are clear and flow freely. On cooling, the polyamide separates out as very fine particles. The method is very suitable for reclaiming scrap nylon. C. O. C.

IV— RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Mechanism of the Reaction of Chlorosulphonic Acid with certain Aromatic Compounds. B. Yu. Yasnitsky. *J. Gen. Chem. U.S.S.R.*, **23**, 107–116 (Jan. 1953).

The main reactions occurring when chlorosulphonic acid reacts with aromatic compounds ($C_6H_5\cdot X$, where X represents various radicals) are—

$$X\cdot C_6H_5 + Cl\cdot SO_3H = X\cdot C_6H_4\cdot SO_3H + HCl \quad (i)$$

$$X\cdot C_6H_5 + Cl\cdot SO_3H = X\cdot C_6H_4\cdot SO_2Cl + H_2O \quad (ii)$$

$$X\cdot C_6H_4\cdot SO_3H + Cl\cdot SO_3H = X\cdot C_6H_4\cdot SO_2Cl + H_2SO_4 \quad (iii)$$

It is considered that the entropy changes occurring in such reactions can be used as measures of relative reaction rates, and ΔS, ΔH, and ΔF are calculated for X = H, CH_3, NH_2, $NH\cdot CO\cdot NH\cdot C_6H_5$, $NH\cdot CO\cdot CH_3$, and $NH\cdot CHO$. For benzene and carbanilide (*s*-diphenylurea), reactions (i) and (ii) should be about equally probable, but for the other compounds (i) should be the main primary reaction, and the sulphonyl chloride formed should result mainly from the slow reaction (iii) of excess of chlorosulphonic acid with the sulphonic acid formed in (i). It is shown also that direct sulphonation by sulphuric acid should

play no significant part when an excess of chlorosulphonic acid is used. These conclusions are confirmed in an experimental study of the kinetics of the reactions of nine aromatic compounds with chlorosulphonic acid.

A. E. S.

New Method of Introducing Fluorine into the Aromatic Nucleus. A. I. Titov and A. N. Baryshnikova. *J. Gen. Chem. U.S.S.R.*, **23**, 346–347 (Feb. 1953).

p-Fluoroaniline is prepared in good yield by adding phenylhydroxylamine to ice-cooled anhydrous hydrofluoric acid and allowing the mixture to stand for two days in the cold. A. E. S.

Oil-soluble Dyes. T. Urahata and H. Hiyama. *Sci. Ind.*, **27**, 15–19 (1953): *Chem. Abs.*, **47**, 4612 (10 May 1953).

Stearic-acid solutions of basic dyes provide brilliant oil-soluble dyes of all hues but of poor fastness with the exception of that from nigrosine. Azo and anthraquinone dyes containing no hydrophilic radicals give fast oil-soluble dyes, the former being yellows, oranges, and reds, and the latter purples and blues. Generally dyes into which a long alkyl chain or fatty acid radical has been introduced turn into oil-soluble dyes more readily, and those which yield oil-soluble dyes with fatty acids do likewise with other solvents; but with some exceptions ability to form oil-soluble dyes with other solvents does not imply the same ability to form them with fatty acids. C. O. C.

***p*-Aminodimethylaniline. VI—Cationoid Halogenations *meta* to a Dimethylamino Group.** J. H. Gorvin. *J.C.S.*, 1237–1241 (April 1953).

Chlorination and bromination of dimethylaniline derivatives in conc. H_2SO_4 in presence of Ag_2SO_4 have given products in which the Cl or Br lies *meta* to the basic group. The applicability of the reaction depends on the nature of the other substituents present. The preparation of 4-amino-3-bromodimethylaniline is described.

H. H. H.

Auxochromic Effect of the Dimethylamino Group and its Coplanarity with the Benzene Ring—I. A. I. Kiprianov and I. N. Zhmurova. *J. Gen. Chem. U.S.S.R.*, **23**, 493–504 (March 1953).

Results already reported are now given with full experimental details, the work being extended to a further group of thiacyanines in which the groups R^1 and R^2 are interchanged (see J.S.D.C., **69**, 33 (Jan. 1953)). The further results are completely analogous to those obtained previously. A. E. S.

Free Radicals in the Decomposition of 1-Benzyl-3-phenyltriazen in Solution. G. A. Razuvaev, E. I. Fedotova, and A. G. Ovchinnikova. *J. Gen. Chem. U.S.S.R.*, **23**, 435–438 (March 1953).

Solutions of 1-benzyl-3-phenyltriazen, one tautomer of which is $C_6H_5{\cdot}CH_2{\cdot}NH{\cdot}N{:}N{\cdot}C_6H_5$, in CCl_4 and in 2-methoxyethanol are heated in presence of Hg until decomp. is complete. In each case benzaldehyde, benzylamine, and benzylaniline are isolated; in CCl_4 only, also phenylmercury chloride; in 2-methoxyethanol only, also acetaldehyde. It is concluded that reaction proceeds both through free radical ($C_6H_5\bullet$ and $C_6H_5{\cdot}CH_2{\cdot}NH\bullet$) formation, and also by intramolecular change (formation of benzylaniline). A. E. S.

Geometrical Isomerism of Azo Compounds. N. Campbell, A. W. Henderson, and D. Taylor. *J.C.S.*, 1281–1285 (April 1953).

cis-2:2′- and -3:3′-Azopyridine are described. In attempts to isolate the *cis* forms of other azopyridine derivatives, numerous cases of polymorphism have been recorded. The thermal behaviour of *cis*-azobenzene is found to be quite different from that of a mixture of azoxybenzene and hydrazobenzene. H. H. H.

Dependence of Molecular Properties of Conjugated Compounds on the State of Electronic Excitation. C. Sándorfy. *Canadian J. Chem.*, **31**, 439–447 (April 1953).

Differences in the electronic arrangements between the ground state and first excited states of some conjugated molecules are discussed in relation to possible changes in reactivity, e.g. in the *cis-trans* isomerisation of azobenzene.

A. J.

Azoic Dyes. X—Brominated Coupling Components. R. V. Talavdekar and K. Venkataraman. *Proc. Indian Acad. Sci.*, **32 A**, 292–303 (1952): *Chem. Abs.*, **47**, 2489 (10 March 1953).

Bromination of some arylides of 3-hydroxy-2-naphthoic acid proceeds as follows. With the anilide, the first Br enters the 4-position, this being readily removed on debromination, the second Br enters the 4′-position, and the third the 7-position. Bromination of the *o*-anisidide gives a mixture of 3′:4- and 4:4′-dibromo derivatives, and a mixture of tribromo derivatives, predominantly the 3′:4:4′ compound. Partial debromination of the dibromo derivatives of the *p*-anisidide gives a mixture of the 7-bromo and the 2′-bromo derivatives, and the tribromo mixture gives the 2′:7-dibromo compound. The 7-bromo derivatives are made by condensing 7-bromo-3-hydroxy-2-naphthoic acid with the appropriate amine.

All the brominated compounds give azo dyes of good brightness and fastness. E. S.

Stabilities of Metal Derivatives of *o*-Substituted Azo Dyes. F. A. Snavely and W. C. Fernelius. *Science*, **117**, 15–16 (1952): *Chem. Abs.*, **47**, 4609 (10 May 1953).

Potentiometric titration revealed the following decreasing stability order for the bivalent metal derivatives of 4-*o*-hydroxyphenylazo-3-methyl-1-phenyl-5-pyrazolone — Cu > Ni > Co > Zn > Pb > Cd > Mn > Mg > Ca > Sr > Ba — and for the tervalent metal derivatives Fe > Cr > Al, both orders agreeing with other results for uni- and bi-dentate groups (13 references), although at a higher stability level. The relative order of azo dye co-ordination power was *oo′*-dihydroxy (azobenzene and arylazopyrazolone) > *o*-carboxy-*o′*-hydroxy > *o*-amino-*o′*-hydroxy > (arylazo)-*o*-hydroxypyrazolone > *o*-hydroxy > *o*-carboxy. The number of metals coordinating with a given class decreases through the list (acidity increasing), with only Cu giving a stable complex with the last.

C. O. C.

Synthesis of Leuco Bases and Dyes of the Triphenylmethane Series—II. I. Kh. Feldman and A. I. Zitser. *J. Gen. Chem. U.S.S.R.*, **23**, 445–449 (March 1953).

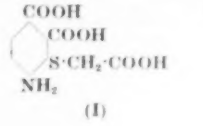
Condensation of 1 mol. of *m*-nitrobenzaldehyde with 2 mol. of guaiacol gives 4:4′-dihydroxy-3:3′-dimethoxy-3″-nitrotriphenylmethane (I), which is converted into a number of related compounds. The fuchsone dye derived from I by oxidation has useful acid–base indicator properties (pH 6·4–7·1: yellow–blue). A. E. S.

Thiocyanation of *o*-Nitroaniline. S. G. Fridman. *J. Gen. Chem. U.S.S.R.*, **23**, 116–118 (Jan. 1953).

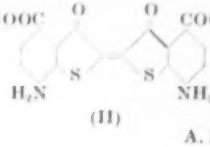
It is shown from data available in the literature and by confirmatory experiments that the product obtained by Blomquist and Diingud (*J. Org. Chem.*, **12**, 721 (1947)) by treating *o*-nitroaniline with ammonium thiocyanate and bromine, regarded by them as 2-amino-4-nitrobenzothiazole, was, in fact, 2-nitro-4-thiocyanatoaniline. Analogous considerations apply to the structures assigned to products obtained from this substance by acetylation and by the Sandmeyer reaction. A. E. S.

Benzothiazole Derivatives. IV—Synthesis of Derivatives of 2-Aminobenzothiazole-5:6- and -6:7-dicarboxylic Acids. I. A. Solovyeva and G. I. Arbuzov. *J. Gen. Chem. U.S.S.R.*, **23**, 489–493 (March 1953).

Dimethyl 4-aminophthalate is treated with KSCN and bromine to yield, via thiocyanato derivatives, a mixture of 2-aminobenzothiazole-5:6- and -6:7-dicarboxylic esters, which are separated by fractional crystallisation from alcohol and converted into the free acids. The 6:7 acid is identified as follows—It is treated with hot conc. alkali, when the thiazole ring is broken, and the amino-mercaptobenzenedicarboxylic acid formed is treated with chloroacetic acid to give I; after undergoing internal condensation and then oxidation, I yields the thioindigo deriv. II, which could not be formed from the 5:6 acid.



(I)

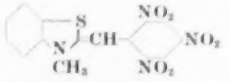


(II)

A. E. S.

Reaction of Quaternary Salts of Heterocyclic Bases with Aromatic Chloronitro Compounds. L. M. Yagupolsky and M. S. Marenets. *J. Gen. Chem. U.S.S.R.*, **23**, 481–488 (March 1953).

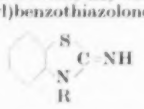
Quaternary salts of 2-methylbenzothiazole, 2-methylbenzoselenazole, and derivatives formed from these by substitution with a variety of groups in the benzene nucleus and in the methyl group, and also a few other related substances, are treated with aromatic compounds containing a Cl, O·CH_3, or S·CH_3 group activated by suitably placed NO_2 groups, e.g. picryl chloride, to give 18 dyes, e.g.—



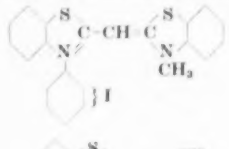
The absorption max. and other properties of the dyes are tabulated. Introduction into the benzene ring of the benzothiazole residue of electropositive groups (e.g. $N(CH_3)_2$, O·CH_3) causes a bathochromic shift in the absorption max.; electronegative groups (e.g. NO_2, CF_3) have the opposite effect. Substitution of CH_3, C_2H_5, or Cl on the methin group produces a considerable bathochromic effect. A. E. S.

Synthesis of Simple Cyanines. G. M. Oksengendler. *J. Gen. Chem. U.S.S.R.*, **23**, 135–139 (Jan. 1953).

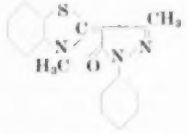
N-Alkyl(or *N*-Aryl)benzothiazoloneimines—

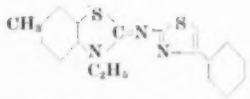


and their derivatives react directly with heterocyclic compounds containing reactive methyl, methylene, or amino groups with elimination of ammonia and formation of cyanine dyes of various types, e.g. monomethin-, *mero*-, and aza-cyanines. The seven new dyes obtained include—



I





A. E. S.

Cyanine Dyes containing Fluorine. II— Cyanine Dyes from Derivatives of 5-Fluoro- and 5-Trifluoromethyl-benzothiazole. A. I. Kiprianov and L. M. Yagupolsky. *J. Gen. Chem. U.S.S.R.*, **22**, 2209–2215 (Dec. 1952).

By the use as intermediates of 5-fluoro-2-methylbenzothiazole and of 2-methyl-5-trifluoromethylbenzothiazole, the syntheses of which are described, three 5:5′-difluoro- and nine 5:5′-bistrifluoromethyl-thiacyanines are prepared, the internuclear chain being varied in length (1–7 methin or substituted methin groups). These 5:5′-substituted dyes, like the 6:6′-difluorothiacyanines (see J.S.D.C., **67**, 199 (May 1951)), differ only slightly in their spectral characteristics from the unsubstituted compounds. A. E. S.

Cyanine Dyes containing Fluorine. III— Cyanine Dyes from Derivatives of 6-Trifluoromethylthiobenzothiazole. A. I. Kiprianov and L. M. Yagupolsky. *J. Gen. Chem. U.S.S.R.*, **22**, 2216–2220 (Dec. 1952).

The syntheses are described of 2-methyl-6-trifluoromethylthiobenzothiazole and 2-amino-6-trifluoromethylthiobenzothiazole, and, by the aid of these intermediates, five thiacyanine dyes containing one or two S·CF_3 groups are prepared. The effect on the absorption max. of substitution by S·CF_3 in the 6-position (or 6:6′-positions) is very slight, whereas substitution by S·CH_3 produces an appreciable bathochromic shift in the one case in which the corresponding methylthio cpd. is known. A. E. S.

Cyanine Dyes. I— Condensation Agents in Syntheses of Cyanine Dyes from Orthoformic Ester. H. Zenno. *J. Pharm. Soc. Japan*, **72**, 1628–1630 (1952); **II— Syntheses of *mero*Carbocyanine Dyes by using Compounds containing Active Methylene Radicals as Condensation Agents.** *Ibid.*, 1630–1633; **III— Syntheses of *mero*Carbo- and Polymethin-cyanine Dyes from Sodium Salts of Formyl Compounds.** *Ibid.*, 1633–1636; *Chem. Abs.*, **47**, 4610–4612 (10 May 1953).

I— Gentle boiling of quinaldine ethiodide with 2-amino-4-methylthiazole and orthoformic ester yielded the bright green 1:1′-diethyl-2:2′-trimethinquinocyanine 1-iodide. Other syntheses of this type are described.

II— Methylbenzothiazole ethiodide boiled for 2 hr. with excess of orthoformic ester yielded the brown 2-(3-cyano - 3 - carbamoylallylidene) - 3 - ethylbenzothiazoline. Syntheses of other pink, brown, and orange dyes of this type are described.

III— Methylbenzothiazole ethiodide, ethyl formylcyanoacetate, pyridine, and piperidine boiled for 45 min. yielded the orange–brown 2-(3-cyano-3-carbethoxyallylidene)-3-ethylbenzothiazoline. Production of other browns, oranges, purples, and greens by similar syntheses is described. C. O. C.

Iminopolymethin Semicyanines. T. Ogata. *Rept. Sci. Research Inst.* (Japan), **27**, 269–274 (1951); *Chem. Abs.*, **47**, 4612 (10 May 1953).

Streptomycin (as a complex $CaCl_2$ salt) was heated for 150 min. at 65° c. in methanol with excess of Mylamiene V (3 - ethylbenzothiazole - 2 - pentamethin - *ω* - aldehyde, obtained from Mylamine V (acetylanilino-2-hexamethinbenzothiazole ethiodide) by direct hydrolysis after its reaction with dipropylamine), then pptd. with ether, filtered under suction, washed with ether (to remove excess Mylamiene V), dissolved in methanol, and crystallised from ether as the complex $CaCl_2$ salt of myceinhexamethinthiocyanine chloride. This gives a brilliant purple solution in methanol. Sodium *p*-aminosalicylate was converted into *m*-aminophenol and then heated with Mylamine V, pptd. with ether, and crystallised from methanol as brilliant green crystals of *m*-hydroxyphenylaminohexamethinthiocyanine iodide. This dye gives a blue solution in methanol. Similarly tryptophanaminohexamethinthiocyanine was obtained as iron-blue crystals (purple soln. in methanol) from tryptophan and Mylamiene V. C. O. C.

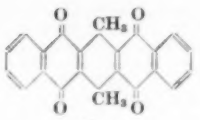
***N*-Bromo(or *N*-Chloro)-*N*-arylsulphonylquinonediimines.** S. I. Burmistrov and L. I. Korochkina. *J. Gen. Chem. U.S.S.R.*, **23**, 94–99 (Jan. 1953).

The cpd. $C_6H_5{\cdot}SO_2{\cdot}N{:}C_6H_4{:}N{\cdot}Hal$ and some of their derivatives formed by nuclear substitution are prepared by treatment of *N*-arylsulphonyl-*p*-phenylenediamines with chlorine or bromine. The unsubstituted cpd. is treated in ammoniacal soln. with phenol to give the violet indophenol $C_6H_5{\cdot}SO_2{\cdot}N{:}C_6H_4{:}N{\cdot}C_6H_4{\cdot}OH(p)$. A. E. S.

Quinones. I— Chloroalkylation. R. H. Thomson. *J.C.S.*, 1196–1199 (April 1953).

1:4-Naphthaquinones (but not benzoquinones) may be chloroalkylated by saturating their solutions in cold acetic acid containing an aldehyde with dry HCl; e.g. 1:4-naphthaquinone gives I, and 2-methyl-1:4-naphthaquinone gives the three derivatives II (R = H, CH_3, and C_6H_5). Catalytic reduction of II followed by oxidation affords diquinones (e.g. III).

(I) (II)



(III)

H. H. H.

Simultaneous Reduction and Chlorination of Aromatic Nitro Compounds in Molten Aluminium Chloride. N. S. Dokunikhin and M. M. Sergeeva. *Doklady Akad. Nauk S.S.S.R.*, **88**, 987–990 (21 Feb. 1953).

It is shown that Scholl cyclisation of 1:5-dibenzoylnaphthalene to 3:4-8:9-dibenzopyrene-5:10-quinone in presence of $AlCl_3$ and a nitro cpd. (e.g. *m*-dinitrobenzene or *p*-nitrobenzoic acid) is accompanied by simultaneous reduction and chlorination of the last substance with formation of e.g. 2:4:5-trichloro-*m*-phenylenediamine or 4-amino-3:5-dichlorobenzoic acid. The reaction is modified in order to afford a good method for the preparation of such chlorinated amines; it is then carried out in a fused mixture of $AlCl_3$ and NaCl, and CuCl or $SnCl_2$ is used as reducing agent in place of 1:5-dibenzoylnaphthalene.

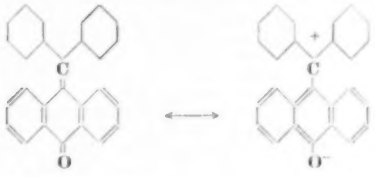
A. E. S.

Formation of 1:2-7:8-Diphthaloylcarbazole by Dehydrogenation of 1:1′-Dianthraquinonylamine. W. Bradley and C. R. Thitchener. *J.C.S.*, 1085–1092 (April 1953).

Both 1:2′- and 2:2′-dianthraquinonylamine react with fused alkali-metal hydroxides to give alizarin as the main product, hydroxylation preceding hydrolysis. 1:1′-Dianthraquinonylamine, however, cyclises to 1:2-7:8-diphthaloylcarbazole, and further action of alkali yields 1:2-phthaloylcarbazole and an acid from which carbazole results on heating with soda-lime. Cyclisation requires the presence of two anthraquinone nuclei, and its rate depends on the alkali; e.g. CsOH ≈ KOH, which is more effective than NaOH. The mechanism of the reaction appears analogous to the formation of di*meso*benzanthronyl from *meso*benzanthrone and of di-(1:9-pyrazoloanthron-2-yl) from 1:9-pyrazoloanthrone (cf. Bradley *et al.*, *J.C.S.*, 1622 (1948); 1247, 1636, 2118 (1952)). H. H. H.

Thermochromism of Diphenylmethyleneanthrone. R. J. W. Le Fèvre and I. Youhotsky. *J.C.S.*, 1318–1319 (April 1953).

The apparent polarities (dipole moments) of cold (pale yellow) and warm (yellow–red) solutions in benzene of diphenylmethyleneanthrone (I) are recorded as 3·77 ± 0·03 D. at 25°C. and 3·93 ± 0·02 D. at 55°C., and indicate marked conjugative modification of the carbonyl group—



(I)

H. H. H.

Fluorescent Brightening Agents. G. Sevens. *Industrie chim. Belge*, **18**, 22–34 (1953): *Chem. Abs.*, **47**, 4618 (10 May 1953).

A review with 117 references, most of them to patents.

C. O. C.

Phototropy of Chlorophyll in Fluid Solutions. R. Livingston and V. A. Ryan. *J. Amer. Chem. Soc.*, **75**, 2176–2181 (5 May 1953).

Oxygen-free solutions of chlorophyll in methanol when illuminated undergo reversible colour changes. Steady illumination (at an "intensity" of ca. 5×10^{9} quanta absorbed per litre per sec.) produced the following changes (measured with bands isolated by interference filters)—For chlorophyll-b, absorption increased at λ = 4030 and 5245 A., and decreased at 4680, 5880, and 6450 A. For chlorophyll-a, absorption increased at λ 4680, 5020, and 5245 A., and decreased at λ 4030, 4395, 5880, and 6450 A. Similar solutions, illuminated with a flash of high intensity and short duration, undergo colour changes whose temporal phase can be followed by photographing a transient trace on an oscilloscope. With scanning light of 4680, 4705, or 4775 A. and a 2×10^{-6} molal chlorophyll-b solution, partial bleaching, of half-life ca. 5×10^{-4} sec., was observed. When the scanning light was 5245 A., increase in absorption was observed. The decay of this change seems to follow a rate law different from that governing the disappearance of the bleaching observed with 4680 A. light, etc. A similar, although less marked, phototropic response was shown by a chlorophyll-a solution scanned at 5245 A. Oxygen inhibits both the flash and the steady-state phototropic changes. These results agree with the following postulates—In addition to the short-lived, singlet fluorescent state, excited chlorophyll can exist in a metastable state (perhaps the lowest triplet state) and as a radical. The radical is formed by the metastable molecule reacting with a molecule of the solvent. Under steady, relatively weak illumination only the radical and normal chlorophyll are present in detectable amounts. Both the radical and the metastable molecule are formed (in comparable concentrations) when the solution is illuminated with a flash of high intensity. The metastable molecules disappear by reacting with normal chlorophyll molecules (or possibly by a simple, first-order decay), while the radicals re-form normal chlorophyll molecules by a second-order reaction.

C. O. C.

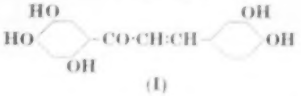
Absorption Spectra of the Ethyl Chlorophyllides. W. F. Watson. *Nature*, **171**, 842–843 (9 May 1953).

The spectra of the two ethyl chlorophyllides in ether and methanol have been measured. The identity of spectral shape indicates that the absorption spectra of the ethyl chlorophyllides are the same as those of the corresponding chlorophylls.

W. R. M.

Chemistry of Extractives from Hardwoods. XI—Isolation of a Diterpene Ester (Methyl Vinhaticoate), and of 6:7:3′:4′-Tetrahydroxyflavanone (Plathymenin), and 2:4:5:3′:4′-Pentahydroxychalkone (*neo*Plathymenin), from *Plathymenia reticulata*. F. E. King, T. J. King, and K. G. Neill. *J.C.S.*, 1055–1059 (April 1953).

Extraction of the heartwood of *Plathymenia reticulata* with light petroleum removes methyl vinhaticoate, and further extraction with ether affords 6:7:3′:4′-tetrahydroxyflavanone (plathymenin) and the corresponding chalkone (*neo*plathymenin) (I), which is the principal crystalline pigment of this deep yellow wood. The last two compounds contain the hydroxyquinol nucleus, which has not hitherto been encountered among natural products of the flavone or *iso*flavone groups.



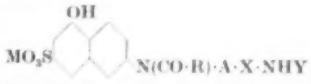
(I)

H. H. H.

PATENTS

Non-diffusing Colour Formers. General Aniline. *BP* 691,989

Compounds of formula—



(A = a radical of the benzene, naphthalene, pyridine, or quinoline series; X = CO, $O{\cdot}CH_2{\cdot}CO$, $CH_2{\cdot}CO$, or $NH{\cdot}CH_2{\cdot}CO$; Y = Alk of > 9 C or an aromatic radical containing an aliphatic chain of > 9 C; M = H or a salt-forming group; R = Alk of < 4 C) are non-diffusing colour formers.

C. O. C.

1-Amino-2-bromo-4-hydroxyanthraquinone. Celanese Corpn. of America. *USP* 2,604,480

1-Amino-2:4-dibromoanthraquinone is heated with 18–70% (preferably 32%) of its wt. of H_3BO_3 in 1·5–6·0 times its wt. of conc. H_2SO_4 for 1 hr. at 150–155°C., and poured into water to give a 98% yield of 1-amino-2-bromo-4-hydroxyanthraquinone.

R. K. F.

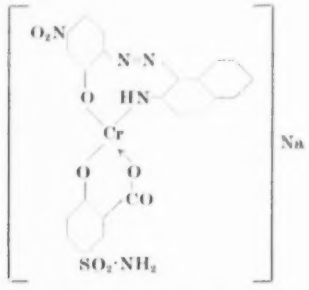
Blue Metal(Chromium)-complex Monoazo Dyes for Wool, Nylon, etc. Ciba. *BP* 692,372

4-Sulphonamides or 4-sulphones of 2:5-dialkoxyanilines are diazotised and coupled with 1-naphtholdisulphonic

acids, and the products converted into chromium complexes, which dye wool, nylon, etc. blue. There is little change in hue in artificial light. Thus the monoazo compound 2 : 5 - dimethoxyaniline - 4 - sulphonamide → 1-naphthol-3:6-disulphonic acid is heated with $Cr_2(SO_4)_3$ under acid conditions in an autoclave at 125–130°C. The resulting chromium complex, formed with de-alkylation of the 2-methoxy group, dyes wool reddish blues the hues of which appear practically the same in artificial light and in daylight. E. S.

Metal(Chromium)-complex Monoazo and Azomethin Dyes. Basf. *BP* 692,073

Chromed azo and azomethin dyes containing 1 atom of Cr to 1 mol. of dye, free from sulpho groups and of, at the most, low solubility in water, may be rendered more soluble by treatment with organic compounds which are not dyes but which form complexes with Cr. The preferred compound of this type is 5-sulphamoylsalicylic acid, but salicylic acid itself and other derivatives of it, *o*-nitrosonaphthols, polyglycols, ethanolamines, etc. may be employed. The products dye animal fibres from neutral or weakly acid baths. Thus the 1 : 1 Cr-dye complex of the monoazo compound 2-amino-5-nitrophenol → 2-naphthylamine is boiled in ethanol with 5-sulphamoylsalicylic acid and sodium acetate until the dye has become soluble. The product dyes wool green from a neutral or weakly acid bath, and is assigned the probable formula—



E. S.

Yellow, Metallisable, Stilbene Disazo Direct Cotton Dyes. S. *BP* 692,465

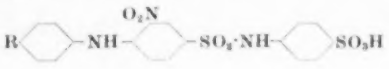
Two molecules of anthranilic acid or its monosulphonic acids (or a mixture of anthranilic acid with its monosulphonic acids) are diazotised and coupled with a dipyrazolone of formula—

(A = H, CH_3, Cl, or Br) to yield yellow disazo direct cotton dyes, which may be metallised in substance or on the fibre. Thus 2 mol. of 4-amino-4′-nitrostilbene-2:2′-disulphonic acid are condensed with 1 mol. of fumaroyl dichloride, and the resulting dinitro compound is converted to the diamine and then the dihydrazine. Condensation with acetoacetic ester then yields the dipyrazolone (A = H), which is coupled in alkaline solution with 2 mol. of diazotised anthranilic acid to give a yellow dye applicable to cotton by the aftercoppering process.

The same dyes may be made by carrying out the reactions of condensation with an acid dichloride, coupling, and metallisation in different orders. E. S.

Diphenylaminesulphonanilides—Dyes for the Solvent Dyeing of Acetate Rayon. Celanese Corpn. of America. *BP* 691,442

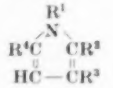
Yellow dyes, suitable for colouring acetate rayon from aqueous-alcoholic sodium thiocyanate and having the formula—



(R = H, Alk, or Alk·O of < 5 C) are made e.g. by condensing 1-chloro-2-nitrobenzene-4-sulphonanilide-4′-sulphonic acid with aniline in presence of aq. sodium acetate. The chlorosulphonanilide is prepared by treating *p*-aminobenzenesulphonic acid with 1-chloro-2-nitrobenzene-4-sulphonyl chloride (from 1-chloro-2-nitrobenzene and chlorosulphonic acid). R. K. F.

Methin Cyanine Dyes. Kodak. *BP* 691,694

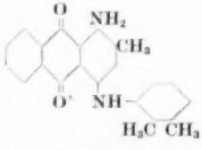
Modification of *BP* 529,440, a simpler and cheaper way of making monomethin dyes being to condense with formic acid a compound of formula—



(R^1 = anilino, Alk, *cyclo*alkyl, Ar, aralkyl, 1-pyrrylalkyl, or 1-pyrrylaryl; R^2 and R^4 each = Alk or Ar; R^3 = H or carbalkoxy). C. O. C.

Sulphonated 2 : 3 - Xylidinoanthraquinones—Wool Dyes. DuP. *USP* 2,605,269

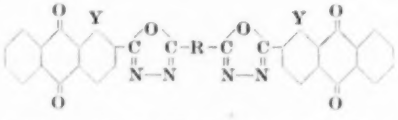
2:3-Xylidine is condensed with 1-methylamino-, 4-bromo-1-methylamino-, 1-amino-4-bromo-2-methyl-, 1-amino-2:4-dihalogeno-, or 1:4-dihydroxy-anthraquinone, and the product sulphonated by treatment in 3–15% oleum for 6–30 hr. at 20–60°C. Thus the compound—



prepared by heating 1-amino-4-bromo-2-methylanthraquinone with 2:3-xylidine and aq. ammonium and copper acetates for 12 hr. at 100–105°c., is treated in 7% oleum for 16 hr. at 20–30°c., and the sulphonated dye separated by diluting to 70% H_2SO_4. R. K. F.

Anthraquinone-Bisoxadiazole Vat Dyes. DuP. *USP* 2,601,179

Red vat dyes of formula—



(R = heteromonocyclic nucleus of 4 or 5 C and O, S, or N; Y = NH_2 or NO_2) are prepared by first condensing 1-amino(or 1-nitro)anthraquinone-2-carboxyhydrazide, prepared by the method of *USP* 2,464,831, with a dicarboxyl dichloride containing the nucleus R, and cyclising the resulting acylated hydrazine. Thus thiophen-2:5-dicarboxyl chloride is heated in nitrobenzene for 2 hr. at 160°c. with 1-nitroanthraquinone-2-carboxyhydrazide. The product is then cyclised by heating at 170–175°c. for 6 hr. in nitrobenzene containing $SOCl_2$. A vat dye is finally obtained by replacing the NO_2 by NH_2 groups by passing NH_3 through a suspension of the nitro compound in nitrobenzene at 175–185°c. R. K. F.

1 - Amino - 2 : 3 - dicyano - 4 - hydroxyalkylamino - anthraquinones—Disperse Dyes. Celanese Corpn. of America. *USP* 2,602,721

The cyano derivatives of *USP* 2,573,732 are reduced to leuco derivatives, which are treated at 40–100°c. for 30 min.–2 hr. in aq. alkali containing a dispersing agent, e.g. ligninsulphonic acid. Aeration precipitates the hydrolysis product, a blue dye having greater affinity for acetate rayon than the original cyano compound. R. K. F.

Leuco Sulphuric Esters. ICI. *BP* 690,682

Vat dyes and anthraquinonoid intermediates are converted to leuco sulphuric esters by first reducing them in an inert organic liquid, e.g. benzene or ethylene dichloride, with a metal, e.g. Zn, in presence of a weakly acidic substance, e.g. phenol or an amide, and a nitrogenous base or quaternary ammonium salt, and then sulphating

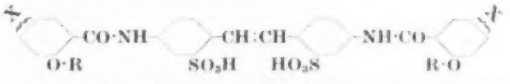
with SO_3 or the addition compound of SO_3 and e.g. a tertiary base or an amide. Thus, all parts being by weight, dibromoanthanthrone (4·65) is heated at 65–70°c. in an inert atmosphere for several hr. with Zn dust (2) and methyltriethylammonium chloride (3·5) in ethylene dichloride (38). After cooling to 0°c., dimethylformamide–SO_3 (10) is added, and the mixture poured, after being stirred for 30 min., into aq. Na_2CO_3. R. K. F.

Isolation of Phthalocyanines. DuP. *USP* 2,602,800

Phthalocyanine pigments of small particle size are obtained from the final reaction mixture of phthalic anhydride, urea, metal salt, catalyst, and inert solvent by adding 1·0–1·5 parts of 85–100% H_2SO_4 per 1 part of pigment and heating at 90–150°c., filtering off the resulting phthalocyanine tetrasulphate, and treating it with aq. alkali. R. K. F.

Fluorescent Brightening Agents. Gy. *BP* 692,346

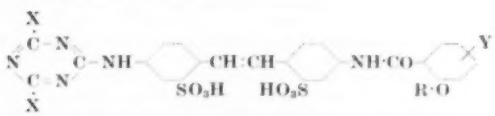
Compounds of formula—



(R = hydroxylated lower alkyl; X = H or CH_3) are fluorescent brightening agents of good affinity for cellulose and good fastness to light. They have good solubility in water and are unaffected by any hardness present; their alkali-metal salts are much less sensitive to salt than are the bis-*o*-alkoxybenzoyl derivatives of 4:4′-diaminostilbene-2:2′-disulphonic acid.

BP 692,347

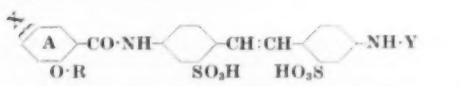
Compounds of formula—



(X = Hal, OH, or preferably NH_2; Y = H or CH_3; R = subst. or unsubst. Alk) have good affinity for cellulose, fastness to light, and intense blue to bluish-green fluorescence.

BP 692,348

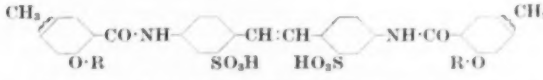
Compounds of formula—



(X = H or CH_3; R = subst. or unsubst. Alk; Y = acyl different from the benzoyl radical A) have good affinity for cellulose, good to very good fastness to light, and pure blue fluorescence.

BP 692,407

Compounds of formula—



(R = unsubst. Alk) are strongly fluorescent on cellulose and have very good fastness to light. C. O. C.

Carbon Black. Columbian Carbon Co. *BP* 692,129–30

A heavy, normally liquid hydrocarbon is used as the raw material for making furnace black by the process of *USP* 2,378,055. C. O. C.

Double Carbonate rich in Lead. La Floridienne, J. Buttgenbach & Cie. *BP* 691,028

Material containing $PbSO_4$ is lixiviated to remove soluble impurities, and the lead is extracted in two stages, the first being treatment with excess of conc. aq. alkali-metal thiosulphate, which separates out SiO_2 and other insoluble impurities together with Sn, As, and Bi, the unstable thiosulphates of which are rapidly decomposed into sulphides. The second stage is treatment with aq. Na_2CO_3, which precipitates the Pb as sodium lead carbonate, while the salts of Ag, Au, and Hg remain in solution. These latter metals are subsequently recovered, and the thiosulphate soln. may be reused. The sodium lead carbonate is particularly suitable for making red lead. C. O. C.

Ultramarines. Usines Guimet and Établissements A. Valuy. *BP* 692,345

Ultramarine is continuously produced in a tunnel furnace having a sand seal, the reaction mixture being carried in trucks along the furnace. The hot gaseous stream in the furnace is prevented from coming into contact with the trucks in the region of the sand seal, where the temperature is such that the SO_2 would damage the metal parts of the trucks, by passing the stream through muffle conduits in the furnace walls, and also introducing hot air or neutral gas into the furnace, in that region. C. O. C.

Luminescent Zinc and Zinc Cadmium Sulphides. British Thomson-Houston Co. *BP* 691,039

In the manufacture of luminescent zinc and/or zinc–cadmium sulphides, use of an alkali-metal phosphate as the flux enables a larger amount of activator to be incorporated and reduces the tendency to change in colour with increase in temperature or to blacken under ultraviolet radiation. C. O. C.

Water-insoluble Non-swellable Organic Pigments. Basf. *BP* 692,654

Treating aqueous suspensions of natural products of starchy or albuminous character with solutions of free hydroxymethyl compounds (in which the hydroxymethyl groups are directly attached to N) in presence of small amounts of acid-reacting reagents and then heating the products for a little while at 110–115°c. yields pigments which do not swell in aqueous liquids even at the boil or in weakly alkaline media. They may be coloured with any desired dye or impregnated with bactericides, plasticisers, surface-active agents, hydrophobic agents, etc., coloration or impregnation being effected during or after treatment with the hydroxymethyl compound. C. O. C.

Luminescent Calcium Halogenophosphate Phosphors. Thorn Electrical Industries and Sylvania Electric Products. *BP* 691,127

Calcium halogenophosphates containing combined chlorine as chloride are prepared by firing mixtures in which all the chloride is present as NH_4Cl, which avoids the use of $CaCl_2$ with the disadvantages due to its being hygroscopic. C. O. C.

Dry Pigments suitable for Direct Incorporation into Viscous Solutions. Ciba. *BP* 691,260

Dry pigments suitable for direct incorporation into viscose or similar viscous liquids are produced by drying a suspension containing an organic or inorganic pigment in the desired particle size, a dispersing agent, and an ether–acid salt of a high-polymeric carbohydrate, e.g. sodium cellulose glycollate, the suspension in 3% aq. soln. having a viscosity of $\leq$ 0·5 poise at 25°c. C. O. C.

N-Acylated Sulphonamides—Textile Assistants and Dye Intermediates (III p. 302).

Our Attainments in the Indigosol Range (VIII p. 310).

System Acetic Acid–Water–Dimethylaniline (XIV p. 313).

New Oxidation–Reduction Indicators. III—*p*- and *m*-*N*-Phenylaminobenzoic Acids. IV—4′-Sulphodiphenylamine-2-carboxylic acid (XIV p. 313).

V— PAINTS; ENAMELS; INKS

Principles underlying the Colour and Appearance of Coatings. E. I. Stearns. *Offic. Digest Federation Paint & Varnish Production Clubs*, (336), 45–69 (1953): *Chem. Abs.*, **47**, 4630 (10 May 1953).

The theoretical basis for much of the optical behaviour of pigments has been worked out. This is true whether one is speaking of light reflected from the surface of a sample or from the interior of a specimen. Improvements in pigment properties can be directed along logical lines, and in many cases the amount of improvement possible can be predicted. C. O. C.

Developments in the Paint Industry for 1952. G. S. Cook. *Paint & Varnish Production*, **43**, (1), 19–32; (2) 19–42, 81; (3) 23–46; 73–90 (1953): *Chem. Abs.*, **47**, 4626 (10 May 1953).

A review. C. O. C.

PATENT

Printing Ink containing a Terpene-modified Phenol–Formaldehyde Resin. Sun Chemical Corpn. *USP* 2,615,854

Inks which, when rapidly heat-dried while still wet or unset, yield prints of gloss at least equal to that obtained by normal air-drying contain a high-boiling aliphatic hydrocarbon solvent, a terpene-modified phenol–formaldehyde resin, and aluminium octoate, there being enough of this last substance to gel the ink. C. O. C.

VI— FIBRES; YARNS; FABRICS

Application of High Compression Stresses to Textile Fibres— I. W. F. Busse. *Text. Research J.*, **23**, 77–84 (Feb. 1953).

The behaviour of cotton fibres when compressed in a random mass at high pressures is investigated. It is shown that great variations in response to high compressions occur, and that these differences may be related to processing and service properties of the fibres. Natural and synthetic fibres are shown to vary over a wide range in their recovery from high compression stresses. A. B.

Application of High Compression Stresses to Textile Fibres— II. H. J. Kolb, H. E. Stanley, W. F. Busse, and F. W. Billmeyer. *Text. Research J.*, **23**, 84–90 (Feb. 1953).

The effect of high compressions on a large number of fibre types is detailed. Rubber, nylon, Saran, wool, Orlon, Vicara, dynel, Dacron, and acetate rayon are investigated, and the possible uses of these measurements are discussed. A. B.

Nature of a Fabric Surface— Thickness–Pressure Relationships. H. Bogaty, N. R. S. Hollies, J. C. Hintermaier, and M. Harris. *Text. Research J.*, **23**, 108–114 (Feb. 1953).

It is shown that the relationship between the thickness t of a fabric and the pressure p applied to it may be described by the relationship $t = a + b/(p + c)$, (a, b, and c = parameters). It appears that b varies directly with the height and density of the surface fibres and inversely with their stiffness. A. B.

Freezing Point Lowering and Solubility Curves of Cellulose Fibres. J. M. Preston and M. V. Nimkar. *Text. Research J.*, **23**, 119–120 (Feb. 1953).

The freezing points of moist cellulose fibres are determined by measuring the cooling curves. When the breaks in the cooling curves are plotted against the concentrations of water, a curve is obtained which is similar to the lowering of freezing point curve of a binary system. A. B.

Magnetic Anisotropy of Cellulosic Materials. L. Loeb and L. A. Welo. *Text. Research J.*, **23**, 251–257 (April 1953).

The measurement of the magnetic anisotropy of fibres by Krishnan's "oscillation" method is described. It is shown that for materials of a given crystalline modification the anisotropy is primarily a function of molecular orientation, but the variation of anisotropy with orientation is different for cellulose I and II. A. B.

Specific Volume of Cellulose in Aqueous Solutions of Inorganic Salts. S. M. Neale and G. R. Williamson. *Nature*, **171**, 842 (9 May 1953).

The curve obtained in the plot of specific volume of cellulose against concentration of salt in aqueous soln. of NH_4Cl, NaCl, and KCl at 25°c. passes through a maximum. In the initial stages of water absorption by cellulose the water is believed to be compressed. Addition of a salt provides polar centres which disorganise the water atmosphere, and it has a decompressing effect on the adsorbed water. The specific volume of the cellulose therefore increases with increasing salt concentration until the activity of the water is so reduced that it is unable to satisfy hydration requirements of salt ions. Further addition of salt results in direct linkage of salt ions with the cellulose, and the specific volume decreases. W. R. M.

Relationship between Various Surface Properties of Wool Fibres. I— Methods for Estimating Wool Fibre Modification. J. Lindberg. *Text. Research J.*, **23**, 67–76 (Feb. 1953).

The effect of alcoholic potash on the epicuticle of wool is studied. It is shown that the mechanical properties and swelling properties of the fibre are not affected. There is no change in the reaction time of treated fibres when the Allwörden reaction is applied. It is shown that the results of most staining reactions are dependent upon the properties of the epicuticle. A. B.

Relationship between Various Surface Properties of Wool Fibres. II— Frictional Properties. J. Lindberg. *Text. Research J.*, **23**, 225–236 (April 1953).

The measurement of coefficients of friction of fibres by means of a modified fibre-twist friction meter is described. It is shown that the with-scale friction of wool fibres treated with alcoholic potash increases with time of treatment. It is likely that the main cause is a chemical change of the surface. The close relationships between friction and breaking strength of top, and between friction and felting rate, are demonstrated. A. B.

Chemical and Physical Properties of Wool in their relation to Wool Processing. G. Nitschke. *Faserforsch. und Textiltech.*, **4**, 162–172 (April 1953).

A review of recent work; 58 references. A. E. S.

Sorption of Hydrogen Chloride by Wool. P. Larose. *Text. Research J.*, **23**, 91–98 (Feb. 1953).

The absorption of hydrogen chloride by wool has been measured at various temperatures from 0° to 42·5°c. and pressures up to 63 cm. of mercury. The isotherms in this range are shown to follow the Freundlich equation. The diffusion coefficient of hydrogen chloride through wool has been calculated, and also the heat of activation. A. B.

The Sequence Glycylalanylglycine in Silk Fibroin. E. Slobodian and M. Levy. *J. Biol. Chem.*, **201**, 371–375 (March 1953).

The tripeptide glycylalanylglycine has been identified in partial hydrolysates of silk fibroin. Analysis by the isotope derivative technique has indicated amounts of this peptide well in excess of the maximum value to be expected from a random arrangement of amino acid residues in silk. P. G. M.

X-Ray Pattern of Sericin and Silk Wax from *Bombyx mori*. E. H. Mercer and F. H. Meyer. *Text. Research J.*, **23**, 243–246 (April 1953).

Several X-ray reflections occurring in raw silk and in some preparations of sericin, previously thought to be characteristic of sericin, are shown to arise from silk wax. A. B.

Infrared Spectra of Model Amides, Polypeptides, and Proteins. E. R. Blout. Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy: *Anal. Chem.*, **25**, 527 (March 1953).

Infrared spectra furnish information regarding the structure of proteins, particularly in terms of the different amounts and types of hydrogen bond. Especially interesting are the location and intensity of the absorptions due to N–H and C=O stretching vibrations, and N–H deformation frequencies close to 3300, 1650, and 1550 $cm.^{-1}$ respectively. These are also observed in amides and polypeptides, some of which may serve as useful models for the study of protein spectra. The infrared spectra of secondary amides of two types of dibasic acid have been studied— (1) compounds such as *NN'*-dibenzylfumaramide, in which hydrogen bonding is only intermolecular, owing to steric restrictions, and (2) compounds such as *NN'*-dibenzylmaleamide, in which there are both inter- and intra-molecular hydrogen bonds. These compounds, and related amides, as well as di-secondary amides of succinic, adipic, suberic, and azelaic acids, have been studied in the solid state, and in soln. in non-hydrogen-bonding solvents where possible. Only one N–H stretching frequency has been found to occur in compounds of type (1), and two such frequencies in those of type (2). Investigation of the infrared spectra of a high-mol.wt. homopolyamide (or polypeptide)— poly-DL-alanine— has also been undertaken, and infrared spectrum data obtained on films of this compound cast from a variety of solvents under varying conditions of temp., salt concn., pH, etc. These results seem to indicate that films cast from this material may be converted from a predominantly intermolecularly to an intramolecularly hydrogen-bonded structure, and that this, under proper conditions, may be reconverted. J. W. D.

Birefringence of Dacron Polyester Fibre. R. G. Quynn and R. Steele. *Text. Research J.*, **23**, 258–259 (April 1953).

The paper of Heyn (*ibid.*, **22**, 513 (1952)) is discussed, and the effect of the degree of drawing on the birefringence is pointed out. A further "wedge" method for measuring birefringence is described. A. B.

PATENTS

Desulphurising and Bleaching Continuous-spun Viscose Rayon. N.V. Onderzoekingsinstituut Research. *BP* 692,023

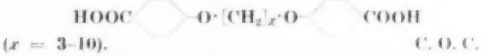
The desulphurising and bleaching of continuous-spun viscose rayon can be carried out very quickly by the usual methods provided that the xanthate ratio of the extruded yarn is reduced to a low value, e.g. by a two-stage process in which the yarn is treated with an aqueous inorganic acid and an inorganic salt until the xanthate ratio is $< 0{\cdot}02$ and, after being washed free from acid and salt, is treated with an aqueous acid until the xanthate ratio is $< 0{\cdot}003$. W. G. C.

Dissolving Keratinous Material and forming Fibres therefrom. Wolsey. *BP* 692,478

Keratinous material is oxidised with an aqueous solution of a sat. aliphatic per-acid of < 5 C at < 100°C. and then dissolved in a hydrotropic solvent, preferably a dilute alkali. There is no severe degradation of the keratin. Filaments can be formed by extruding the solution into strong solutions of electrolytes, into acids, or into aqueous solutions of alcohols or ketones. C. O. C.

Linear Polyamides. ICI. *BP* 691,278

Linear polyamides of excellent resistance to degradation on exposure to light are produced from diamines and compounds of formula—



($x = 3$–10). C. O. C.

Heat-setting *N*-Alkylpolyamide Yarns. ICI. *BP* 692,069

The highly elastic yarns formed from polyamides containing *N*-alkyl(e.g. *N-iso*butyl)-substituted polyamides are set by annealing at 60–80°C. for > 3 sec. and then heating at 90–100°C. for a longer time. This reduces the shrinkage on treating in boiling water to 2–5% and does not weaken the yarn. W. G. C.

Non-linear Polymers capable of being drawn into Filaments. Wingfoot Corpn. *USP* 2,615,863

The non-linear polyamides prepared by condensing polybasic amines containing > 2 reactive amino groups with amino acids containing only one amino and one carboxylic group are thermoplastic and can be drawn into useful, strong fibres. C. O. C.

Fibre-forming Copolymers of Vinylidene Cyanide. B. F. Goodrich Co. *USP* 2,615,865–80

Copolymers useful for forming filaments and films are obtained from vinylidene cyanide and mono-olefins, vinyl esters of aliphatic or aromatic monocarboxylic acids, subst. or unsubst. styrene, vinyl or vinylidene chloride, alkyl methacrylates, halogenated 1:3-butadienes, conjugated aliphatic diolefins, propylene, *iso*propenyl esters of organic monocarboxylic acids, vinyl esters of *α*-halogeno sat. aliphatic monocarboxylic acids, halogenated mono-olefins, 1:2-dihalogenoethylenes, or alkyl acrylates. C. O. C.

Polyacrylonitrile Spinning Solutions. Chemstrand Corpn. *BP* 692,462

The viscosity of organic solutions of acrylonitrile polymers is reduced by adding 0·1–5% on the weight of solvent of calcium chloride, lithium bromide, sodium thiocyanate, or magnesium bromide. W. G. C.

Acrylic Fibres with Wool-dyeing Properties. Monsanto. *BP* 692,376

The dyeing affinity of acrylic fibres is improved by incorporating in the polymer 2–40% of another polymer containing vinylpyridine or alkyl-substituted vinylpyridine, the pyridine nuclei being quaternised by reaction with an alkyl ester of an oxygen-containing sulphur acid, e.g. methyl toluenesulphonate. W. G. C.

Synthetic Polypeptide Fibres. Courtaulds. *BP* 692,433

Fibres of synthetic polypeptides made by polymerising anhydrocarboxyamino acids are insoluble in non-polar organic liquids, e.g. benzene, after being treated in an aliphatic monocarboxylic acid having 1–6 C atoms or a like acid having on the *α* carbon atom Br, C_6H_5, or SH, so that at least part of the fibres is converted into the *β* molecular configuration. W. G. C.

Rubber Filaments. Dunlop Rubber Co. *BP* 692,040

Filaments suitable for the manufacture of fabrics where abrasion resistance is important are made by stretching latex-cyclised rubber at a temperature at which it is rubbery, and then cooling in the stretched state to a temperature at which it is no longer rubbery. W. G. C.

Fibre-forming Polymers from Azelaic Dihydrazide and Oxalic Acid. Celanese Corpn. of America. *USP* 2,615,862

Thermoplastic nitrogenous polymers, suitable for forming filaments, foils, etc., are obtained by reaction of an aliphatic, alicyclic, aromatic, or araliphatic dicarboxylic acid with an aliphatic, alicyclic, or aromatic dihydrazide in a neutral or inert organic solvent at polymerisation temperature. C. O. C.

Felting in Laundering of Wool Blends (VII this page).

Dyeing Phenomena in Fibres in relation to their Crystalline Structures. I— Crystalline Regions of Cellulose Fibres. II— Fibrillation of the Crystalline Regions of Cellulose Fibres (VIII p. 310).

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Felting in Laundering of Wool Blends. H. Bogaty, A. M. Sookne, L. I. Weiner, and M. Harris. *Text. Research J.*, **23**, 114–118 (Feb. 1953).

The felting of wool blended with nylon, Vicara, and viscose rayon has been studied. It is shown that felting during laundering decreases as the proportion of nylon is increased, but that the incorporation of viscose rayon tends to increase the feltability. Vicara blends are intermediate in behaviour. This may be explained by the relative ease of deformation of the various fibres. A. B.

Properties of Freshly Formed Surfaces. XVIII— Dynamic Surface Potentials and the Adsorption Process: Molecular Orientation in Soluble Films of Decyl Alcohol. C. C. Addison and D. Litherland. *J.C.S.*, 1143–1150 (April 1953).

An apparatus is described for the study of continuous changes in potential at fresh surfaces. With solutions of decyl alcohol, when concentration equilibrium is established between the surface and bulk solution, the surface tension shows no further change, but surface potential changes occur which are interpreted as reflecting the rate of orientation of the disoriented film produced immediately adsorption is complete. Unlike surface tension, which is relatively insensitive to changes in orientation, the surface potential of a solution depends as much on the condition of the adsorbed film as on the surface excess. H. H. H.

PATENT

Washing Raw Wool. Separator AB. *BP* 691,648

Wool is washed in a washing machine with a hydrocarbon solvent, e.g. an aliphatic hydrocarbon containing 5–10% by wt. of aromatic hydrocarbon and having a flash point of 45–48°C., at a temp. of 30–35°C., after which the solvent is removed and its temp. is raised to 70–120°C. to dissolve fully all separated waxes. The solution is then supercooled and returned to wash fresh wool, with, if necessary, an intermediate treatment with water to remove suspended matter from the solvent. A portion of solvent is removed for separation of dissolved waxes, e.g. by distillation, so that the wax content of the washing solvent is kept below a certain concentration when this purified liquor is returned to it. J. W. B.

VIII—DYEING

Our Attainments in the Indigosol Range. F. Defalque. *Industrie textile*, **69**, 683–687 (1952): *Chem. Abs.*, **47**, 4612 (10 May 1953).

The historical development of the Indigosols is reviewed. The low affinity of some of the range can be improved by pretreating the fibres with cation-active agents, which form insoluble compounds with Indigosols. Details are given of the application of Indigosols to cotton, viscose rayon, animalised viscose rayon, acetate rayon (without use of solvents or swelling agents), wool, silk, Rhovyl, Thermovyl, nylon, Perlon, asbestos, glass fibres after albumin treatment, and acetate–viscose rayon, acetate rayon–cotton, and wool–cotton blends. C. O. C.

Sulphur Dyes. XXX—Sodium Sulphide needed in Dyeing. H. Hiyama, H. Ikegami, and O. Manabe. *Sci. Ind.*, **27**, 6–7 (1952): *Chem. Abs.*, **47**, 4612 (10 May 1953).

With Immedial Indone R ($C_{28}H_{16}O_4N_4S_5,H_2O$) 21·7% (on the wt. of dye) of Na_2S was needed for complete reduction to the leuco base, 10% for replenishing the loss of Na_2S in the bath by atmospheric oxidation, and 41·7% for adsorption of dye on to the fibre (here Na_2S could be largely replaced by NaOH or Na_2CO_3 if the pH was kept at 10·6). It thus seems possible that the usual consumption of Na_2S, 2·3 times that of the sulphur dye, may be reduced by altering the liquor and/or method of dyeing. C. O. C.

Dyeing Phenomena in Fibres in relation to their Crystalline Structures. I—Crystalline Regions of Cellulose Fibres. K. Miyasaka. *J. Soc. Textile Cellulose Ind.* (Japan), **8**, 551–554 (1952); **II—Fibrillation of the Crystalline Regions of Cellulose Fibres.** *Ibid.*, 554–556: *Chem. Abs.*, **47**, 4601 (10 May 1953).

I—Determination (by Maeda's method) of the crystalline regions of seven kinds of natural and regenerated celluloses and microscopic examination of their structures in residual solutions showed cotton to have the highest crystallinity (80·3%) and tyre-cord rayon the lowest (45·1%). High crystallinity (showing microscopically flaky and twisted rods) seems to be associated with more resistance to mechanical and chemical treatments (including dyeing) than lower crystallinity (showing microscopically straight rods).

II—With suitable swelling agents or with mechanical stirring, the crystalline regions of all the fibres fibrillated (more with higher crystallinity) along the direction of micellar orientation. Fibrillation was generally reticular in natural fibres and parallel to the fibre axis in regenerated fibres. C. O. C.

PATENT

Improving the Fastness Properties of Dyeings or Prints produced with Water-soluble Direct Cotton Dyes. Ciba. *BP* 691,686

Dyeings and prints produced with water-soluble direct cotton dyes which contain sulphonic acid or carboxyl groups, and which either contain copper in complex combination or will form complexes with copper, have their fastness improved by treatment with an aq. soln. of a condensate of an aldehyde with a compound containing at least one $>N\cdot C(:\dot{N})\cdot N<$ group, the condensate being produced in presence of 0·1–1·0 equivalent of an acid for each molecule of the compound containing the above group. The treatment can be carried out before or during any necessary coppering. C. O. C.

Laboratory High-temperature Dyeing Unit (XIV p. 315).

IX—PRINTING

Efficiency of Vat-dye Ageing depends on Temperature Control. T. N. Patrick. *Textile World*, **103**, 147, 236, 238, 240, 242 (June 1953).

The point of maximum absorption of water from the steam atmosphere in the ager is between 100 and 94% R.H. at 212 and 216°F. Rise in temperature from other causes lowers the R.H. and hence the solubilising power of the steam, which in turn brings about decomposition of some vat dyes, reduces the colour yield by limiting transfer of dye from printing paste to fibre, and dulls the colour. It is necessary to condition or cool vat-printed goods before ageing in order to dissipate the heat of drying of the prints and increase the moisture regain to normal. If warm, dry, printed cloth is introduced into the ager, the heat of drying must be dissipated before conditioning of the material can occur. If not dissipated, this heat will slow down the condensation of water vapour in contact with the fabric and the print colour. Marked rise in temperature occurs. C. O. C.

PATENTS

Photographic Printing on Textiles. Collux. *USP* 2,615,381

Cloth treated with a light-sensitive dye is fed between a conveyor belt and a revolving glass cylinder, the latter being suspended along part of its periphery by the belt. A tensioning roller between the feed roller and the cylinder provides smudge-free contact between the cloth and the glass cylinder. A printing pattern is attached to the cylinder. Inside the cylinder there are radiant heating and illuminating means and a reflector. Above the cylinder there are an air flue and cooling means. A moistened wiping device is in peripheral contact with the cylinder. C. O. C.

Colour Photography. H. von Fraunhofer and H. E. Coote. *BP* 691,962

Modification of *BP* 682,061 (J.S.D.C., **63**, 37 (Jan. 1953)), the layer of emulsion containing the magenta colour former being replaced by two red-sensitive silver halide emulsion layers each approx. half as thick as the layer containing the blue–green colour former. These two layers contain, respectively, a magenta colour former and a yellow colour former. After exposure, this positive material is developed as described in the parent specification. C. O. C.

Direct Production of Positive Multicoloured Photographic Images and of Coloured Masks in a Colour-photographic Film. FBy. *BP* 690,996–7 C. O. C.

Coupling Components for Colour Photography. ICI. *BP* 691,102

Use of finely dispersed insoluble coupling components obtained from water-soluble compounds containing no anionic solubilising groups but containing one or more CH_2X groups (X = ternary or quaternary salt group), or use of such water-soluble compounds followed by insolubilisation after coupling, enables satisfactory dispersions to be obtained, which have no tendency to displace the optical sensitisers. C. O. C.

Improving the Fastness Properties of Dyeings or Prints produced with Water-soluble Direct Cotton Dyes (VIII this page).

X—SIZING AND FINISHING

Excessive Wettability. P. Winckler. *Industrie textile*, **69**, 567–568 (1952): *Chem. Abs.*, **47**, 4617 (10 May 1953).

Excessive wettability of fabrics may be very disadvantageous in service. It occurs mainly when alkaryl detergents are used. It may be overcome by (1) neutralising the residual anionic and cationic agents by cationic or anionic compounds respectively, (2) eliminating residual alkyl sulphates by soaping, and (3) slight hydrophobic treatment. C. O. C.

PATENTS

Rendering Cotton and Linen Cloths Crease-resisting. Joseph Bancroft & Sons. *BP* 692,184

The fabric is impregnated with an aqueous polybasic acid, e.g. orthophosphoric acid, and a nitrogenous compound basic toward the acid, e.g. urea, and baked to bring about esterification of the cellulose. Finally, mercerisation restores the strength lost by esterification. The finished fabric has superior crease-resistance accompanied by a soft, supple handle. C. O. C.

Crimping Textile Fibres. Alexander Smith. *BP* 692,236

Permanent artificial crimp is imparted to textile fibres by passing them through a crimping zone, in which they are mechanically folded by fluted feed rollers or by a fluted conveyor, into a container where they are held under pressure, e.g. by forcing a piston down on to them, and

where a setting agent such as steam at 20 lb./sq.in. is introduced. Alternatively the operation can be combined with forced-circulation dyeing, the hot dye liquor acting as the setting agent. J. W. B.

Modifying Keratin. Procter & Gamble Co. *USP* 2,615,782–3

Keratinous substances can be chemically and physically modified, e.g. hair can be permanently set, while retaining disulphide bonds, by reducing the keratin and then treating with an organic thiosulphuric acid or thiosulphate. *USP* 2,615,828

When a thiol of formula R^1SH is used as the reducing agent for keratin, the presence in the solution of a compound of formula $R^2{\cdot}S{\cdot}SO_3H$ (R^1 and R^2 = univalent radicals containing no carboxy or amino group and linked to the S atom through C) softens the fibre without damaging it even when in contact with it for a long time. C. O. C.

Reducing the Tendency of Wool to Shrink. Stevensons (Dyers). *BP* 692,258

Treatment with aqueous permonosulphuric acid or a salt thereof at pH not within the range 2–7, and if the pH is < 2 in presence of ≤ 10% by wt. on the solution of sulphuric acid, reduces the felting power of wool without obvious damage to the wool while retaining the original handle and colour. C. O. C.

Reducing the Felting Power of Wool and Increasing its Resistance to Abrasion. Commonwealth Scientific and Industrial Research Organisation. *BP* 692,380

The tendency to felt of materials containing wool is greatly reduced by treating them with a solution in an organic solvent of a synthetic linear polyamide substituted by alkoxymethyl or hydroxymethyl groups attached to the peptide N and then removing these substituents, e.g. by treating the impregnated material with a mineral acid. This treatment also increases the abrasion resistance of the material. *BP* 692,381

Before or during impregnation with the polyamide the material is treated with an alkali-metal hydroxide dissolved in an organic solvent. C. O. C.

Setting of Nylon Yarns. Adshead & Geeson. *BP* 692,637

The yarn is passed either continuously or intermittently through steam and then hot dry air, and when the yarn is dry it is passed over and in contact with a surface heated to ≤ 300°F. The steam is superheated or not, according to the temperature and amount of moisture needed to obtain the desired extensibility of the yarn. C. O. C.

Imparting Water-resistance to Textiles. U.S. Secretary of the Army. *USP* 2,615,824

Superior water-resistance is imparted to textiles by treating them with a compound of formula $Alk{\cdot}SiHCl_2$ or $Alk{\cdot}SiHBr_2$ dissolved in an inert solvent, and then hydrolysing and condensing the silane. C. O. C.

Cropping. George Spencer. *BP* 691,018

Tubular fabric is cropped by passing it in tubular form to a cropping blade, the tube being flattened and smoothed so that it reaches the blade in flattened condition and one face can be cropped. C. O. C.

Coating of Fabrics. FBy. *BP* 692,045

Coating without undue penetration, particularly when di*iso*cyanate-modified esters are used as the coating material, is effected by pretreating the fabric with water or an aqueous aliphatic diamine or amino-alcohol, coating while still moist, and then, if desired, treating with water, water vapour, an aqueous aliphatic diamine, or an aliphatic diamine vapour. C. O. C.

Coating of Webs. Herts Pharmaceuticals. *BP* 691,182

Fabric is coated, while selected areas are left uncoated, by placing blanks of magnetic material on such areas, holding the blanks in position by magnetic force while coating the fabric and the blanks, and finally removing the blanks. C. O. C.

Coating with Fibres. A. R. Hug. *BP* 691,061

An electric field is used to move the fibres toward the object to be coated (which has previously been coated with an adhesive), one pole of the source producing the field being connected to the object. The method is suitable for the treatment of strings, sheets, etc. C. O. C.

Laminated Flexible Material from Rayon Fibres. Minnesota Mining & Manufacturing Co. *BP* 691,888

A rayon fabric consists of a tissue-like web serving as a base layer and formed from carded 1 in. staple viscose and plasticised acetate rayon fibres, the last being 50–65% by wt. and so arranged that they form a network entrapping the viscose fibres, on one side of which is a monolayer of non-plasticised cellulose acetate continuous filaments which bond to the plasticised fibres. The whole is impregnated with flexible water-resistant sizing, which superficially coats the yarns without greatly stiffening the fabric and gives a high sheen on the yarn side. The material is useful for slitting into strong resilient decorative ribbons. J. W. B.

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Chemical Changes produced in the Cellulose Macromolecule by Oxidising Agents. VIII—Oxidation of Cellulose by Hydrogen Peroxide. V. I. Ivanov, E. D. Kaverzneva, and Z. I. Kuznetsova. *Izvestiya Akad. Nauk S.S.S.R. Otdel. khim. nauk*, 374–384 (March–April 1953).

The results of this work, now given *in extenso* with experimental details, have been reported previously (see *J.S.D.C.*, **69**, 70 (Feb. 1953)). A. E. S.

PATENTS

Coating Compositions for Photographic Paper. Kodak. *BP* 692,105

A photographic light-sensitive paper comprises a paper support, a substratum baryta layer, and a light-sensitive silver halide emulsion layer coated over the baryta, the substratum baryta layer being formed with an aqueous suspension of $BaSO_4$ and a binder consisting of 25–100% of styrene–butadiene copolymer, the percentage being the proportion of dry weight of copolymer to total dry weight of binder used. The ratio of the dry weight of $BaSO_4$ to the dry weight of total binder is 5–20 : 1. The $BaSO_4$ suspension may contain 462 parts of $BaSO_4$, 36 of styrene–butadiene copolymer, and 12 of gelatin (all dry weight). S. V. S.

Moistureproof Coated Sheets and Films. British Cellophane. *BP* 692,154

Moistureproof coated sheets or films are prepared by applying an aqueous dispersion of a vinylidene chloride copolymer to non-fibrous hydrophilic sheet or film, e.g. regenerated cellulose, in a sufficiently thin layer for the water to be wholly absorbed by the base, the dispersed copolymer coalescing to form a smooth, transparent, moistureproof surface coating, which is then dried to > 8% moisture content (based on bone-dry weight of sheet) and fused. The aqueous dispersion of the copolymer may include a small proportion of an acid sulphate of a normal aliphatic alcohol of 12–24 C. 0·01–5·0% of the sulphate, which may be *n*-octadecyl hydrogen sulphate, may be employed (based on the initial weight of the monomers from which the copolymer is formed). The copolymer dispersion may also include 0·05–0·30% (calculated on monomer weight) of a liquid aqueous colloidal dispersion of a substantially water-insoluble inorganic compound, e.g. silica or alumina. The proportion of acid sulphate to inorganic compound, which together improve the slipperiness of the moistureproof film, is 10–40 : 1. The copolymer is prepared by polymerising a mixture of at least 4 parts by weight of monomeric vinylidene chloride and 1 part of monomeric methyl methacrylate or acrylonitrile, or a mixture of at least 2 parts by weight of monomeric vinylidene chloride and 1 part of monomeric vinyl chloride. To promote adhesion of the coating to the base film in the presence of water the polymerisable mixture also includes 0·1–2·5% by weight of the total monomeric charge of one or more of the acidic ethylenic compounds citraconic acid, citraconic anhydride, itaconic acid, itaconic anhydride, mesaconic acid, and acrylic acid, or a mixture of acidic anhydrides, including citraconic and itaconic anhydrides, obtainable from citric acid by distillation. S. V. S.

Rapid Method for the Estimation of the Readily Accessible Portion of Cellulose (XIV p. 314).

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Absorption Spectrum of the Peptide Bond. II—Influence of Chain Length. A. R. Goldfarb. *J. Biol. Chem.*, **201**, 317–320 (March 1953).

The absorption spectra of polylysine (n = 6, 14, 33, 48, and 53) and polyornithine (n = 35) are reported. The molar absorption coefficient (ϵ_m) *versus* pH curves for hexalysine and triglycine are reported at between about pH 1 and 7. The change in ϵ_m is correlated with the ionisation of the carboxyl group. It is concluded that the contribution of each peptide group ϵ_p is smaller for the smaller peptides and rises to a constant value. P. G. M.

Synthesis of Glyconyl Peptides. D. G. Doherty. *J. Biol. Chem.*, **201**, 857–866 (April 1953).

A new class of carbohydrate amino acids has been synthesised, viz. aldonic acids coupled through their carboxyl group to the α-amino group of amino acids in a stable CO–NH linkage. These compounds have been prepared by coupling the acetylated aldonoyl chloride with the amino acid ester hydrochloride, free amino acid ester, or the amino acid. The acetylated glyconyl peptide derivatives have been subjected to the usual reactions to yield glyconyl peptide esters, glyconyl peptide amides, and free glyconyl peptides. P. G. M.

PATENT

Suède Leather. FBy. *BP* 692,450

Improved fibre formation for the nap finish is obtained by treating the surface of the leather with an aqueous soln. or dispersion of a resin-former containing N and a CH_2OH or NCO group and capable of condensing by itself, e.g. the precondensate of a urea–formaldehyde resin (1 : 2·5 mol.) or hexamethylene di*iso*cyanate. C. O. C.

Determination of the Sequence of Amino Acids in Peptides and Proteins. I—Preparation, Properties, and Chromatographic Adsorption of the Azobenzene-*p*-sulphonyl Derivatives of Various Amino Acids (XIV p. 314).

XIII—RUBBER; RESINS; PLASTICS

Nomenclature and Classification of Macromolecular Compounds. V. V. Korshak. *Izvestiya Akad. Nauk S.S.S.R. Otdel. khim. nauk*, 321–335 (March–April 1953).

A review is made of existing systems for the classification and nomenclature of macromolecular compounds, and a system of classification based on the chemical nature of the fundamental chain is proposed, there being two main categories, comprising carbochain and heterochain compounds respectively; these are divided according to the chemical nature of the members of the chain, and the classes formed are subdivided according to the nature and disposition of the side groups. The author's system of nomenclature is expounded (cf. J.S.D.C., **69**, 226 (June 1953)), and examples of the classification and naming of numerous polymeric substances are given in tabular form. A. E. S.

Effect of Heat and Light on Polyvinyl Chloride. D. Druesdow and C. F. Gibbs. *Modern Plastics*, **30**, (10), 123, 124, 126, 128, 216, 218, 221, 222 (May 1953).

The thermal degradation of polyvinyl chloride is primarily a dehydrochlorination reaction. In an atmosphere of nitrogen the rate tends to become steady and is not affected by a build-up of HCl. The intrinsic viscosity of the polymer increases with its dehydrochlorination. If oxygen is present, the rate increases with time and the reaction is autocatalytic with respect to HCl. Drop in intrinsic viscosity in the early stages of degradation followed by increase indicates that chain scission and cross-linking are competing reactions when oxygen is present. Heavy-metal stabilisers absorb HCl in an atmosphere of nitrogen, but when oxygen is present they appear to function through some other mechanism. Exposure to ultraviolet radiation at room temperature results in evolution of small amounts of HCl with simultaneous absorption of measurable quantities of oxygen. The irradiated polymer is more susceptible to thermal degradation than the original. Possible mechanisms for these reactions are discussed. C. O. C.

PATENTS

Heat Setting of Films of Vinylidene Chloride–Vinyl chloride Copolymers. Dow Chemical Co. *BP* 692,429

Films having low shrinkage at 100°C. are obtained by heating a copolymer of vinylidene chloride and vinyl chloride at $\geq$ 10°C. below its softening point whilst allowing it to shrink under controlled conditions, and then cooling it to $<$ 100°C. under sufficient tension to prevent further shrinkage.

BP 692,430

An improved process consists in heating the film at 20–40°C. below the softening point for 30–120 sec. while holding the film to prevent shrinkage, releasing the tension sufficiently to allow the article to slip while heating for a further 30–120 sec. at between 100 and 20°C. below the first temperature, and finally cooling to $<$ 100°C. W. G. C.

Cast Pigmented Plastic Sheet. W. W. Ulmer and L. R. Burroughs. *USP* 2,615,271

Production of a cast synthetic-resin sheet of uniform thickness and continuous integral structure and pigmented throughout is described. The density of the pigment in the sheet varies to form a design, the parts of greatest pigment density coinciding with ripples formed on one of the surfaces of the sheet. C. O. C.

Floor Coverings. Chemische Werke Hüls. *BP* 692,444

Floor coverings, which unlike linoleum require no fabric base, are produced by using as binder for the filler polymers of 55–90% of styrene and 45–10% of butadiene. They have a smoother surface and better resistance to abrasion and water, and are more flexible and stronger, than similar materials made from linseed oil or dicarboxylic acid–polyhydric alcohol condensates. Used in conjunction with these two latter types, the advantages of the two are obtained without their disadvantages. Used in conjunction with linseed oil types, they reduce the drying time from 4–6 weeks to about 5 days. C. O. C.

Polymers of Acryloyltriazine–Aliphatic Amine Reaction Products (III p. 302).

Solvents for Linear Polyamides (III p. 302).

XIV—ANALYSIS; TESTING; APPARATUS

Direct Titrimetric Determination of Fluoride in Natural Waters. A. M. Bond and M. M. Murray. *Biochem. J.*, **53**, 642–645 (March 1953).

A method for the estimation of fluoride in natural waters by titration with thorium nitrate at pH 3·3, using sodium alizarinsulphonate as indicator, is described. Interfering anions are first removed by addition of $BaCl_2$ and filtration. Calcium and magnesium in concentrations found in hard waters do not interfere. P. G. M.

Determination of Low Concentrations of Copper. J. K. Brown and J. C. Connell. Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy: *Anal Chem.*, **25**, 519 (March 1953).

The procedure of McCurdy and Smith (*Analyst*, **77**, 846 (1952)) is modified, in that 100 ml. of sample buffered to pH 4·2 is extracted once with 10 ml. of ethylene dichloride containing neo-cuproine, the ethylene dichloride is drawn off, and 0·5 ml. of *iso*propanol is added to clarify the soln. The solvent is then measured in a spectrophotometer, and the optical density read at 454 mμ. There is a straight-line relationship between p.p.m. Cu and optical density. With care, 0·001 p.p.m. Cu can be determined. J. W. D.

New Colorimetric Reagent specific for Copper—Determination of Copper in Iron. G. F. Smith and D. H. Wilkins. *Anal. Chem.*, **25**, 510–511 (March 1953).

The new reagent—2:9-dimethyl-4:7-diphenyl-1:10-phenanthroline (to which the authors give the trivial name "batho-cuproine")—is specific for Cu, and does not chelate with Fe, even in the presence of a large excess; it has a high mol. extinction coefficient, viz. 14,160. J. W. D.

Colorimetric Determination of Magnesium with Eriochrome Black T. A. E. Harvey, J. M. Komarmy, and G. M. Wyatt. *Anal. Chem.*, **25**, 498–500 (March 1953).

The use of Eriochrome Black T represents the only colorimetric method for determining Mg which involves a

true soln. of a coloured Mg complex, the colour density of which $\propto$ [Mg]. The dye, itself blue in methanol soln., forms a soluble, intensely red, and very slightly dissociated complex with Mg within the pH range 7–10. At pH 7·75 the absorption curves of dye and complex merge; the determination is thus carried out at pH 10·1, this being secured by an NH_4Cl–NH_4OH buffer. The absorbance at 520 mμ. is measured. The dye gives also a complex with Ca, and this gives an absorption curve similar to that of the Mg complex. The absorbance of the soln. of the Mg complex alters significantly on ageing, but the effect is negligible at 520 mμ., and is most marked at longer wavelengths. J. W. D.

Differential Titration of Amines. J. S. Fritz. *Anal. Chem.*, **25**, 407–411 (March 1953).

A solvent suitable as a medium for the differential titration of amines must—(1) Have no pronounced basicity which will interfere with the titration of weak bases such as aromatic amines; water and alcohol fail in this respect. (2) Have no pronounced acidity which will tend to level most amines to about the same basic strength; acetic acid does not satisfy this requirement. (3) Have a sufficiently high dielectric constant to allow the titration to be followed potentiometrically. Acetonitrile satisfies these requirements. The amine soln. is titrated with a dioxan soln. of $HClO_4$ (which is unstable in acetonitrile), this method showing much decreased sensitivity in differentiation amongst amines of $pK_b < 6$ (as against 9·5 when acetic acid is used as solvent). Three procedures are described—(i) potentiometric, (ii) using visual indicators, as can often be done once a given mixture has been titrated by (i), (iii) using acetic acid as solvent; this is applicable to weak bases such as aniline, *o*-chloroaniline, sulphathiazole, and pyridine, since these are too weak to be levelled by acetic acid. Aliphatic primary and secondary amines may be differentiated by treating the mixture with salicylaldehyde, which reacts with primary amines to form weaker bases (which can still be titrated). J. W. D.

High-frequency Titrations of Organic Bases—in Glacial Acetic Acid with Perchloric Acid. W. F. Wagner and W. B. Kauffman. *Anal. Chem.*, **25**, 538–540 (April 1953).

The results of high-frequency titrations of organic bases (the paper reports the study of aniline, *p*-toluidine, pyridine, and *NN'*-bis-β-cyanoethyl-2:5-dimethylpiperazine) in glacial acetic acid with perchloric acid agree well with those obtained by potentiometric and visual end-point methods, and the disadvantages of inadequate visual indicators and electrode systems when working in non-aqueous media are eliminated. The method, which has not been found to be applicable to *o*- or *p*-nitroaniline, or to urea, is given in detail. J. W. D.

System Acetic Acid–Water–Dimethylaniline. L. Garwin and P. O. Haddad. *Anal. Chem.*, **25**, 435–437 (March 1953).

Ternary mixtures of acetic acid, dimethylaniline, and water may be analysed simply by determining the refractive index, titrating the acetic acid directly with standard alkali, and referring to standardisation curves (liquid–liquid equilibria at 25°c. and n_D^{25} as a function of composition) given in the paper. The marked difference between the refractive indices of dimethylaniline and water makes this property a sensitive measure of dimethylaniline content. Water is determined by difference. J. W. D.

Differentiation of Chelating from Non-chelating Phenols. S. Soloway and P. Rosen. *Anal. Chem.*, **25**, 595–598 (April 1953).

The ferric complexes of chelating phenols are stable over wider ranges of pH than those of non-chelating phenols. The stability of the phenolic–ferric complex varies also with the solvent. By the use of acetic acid or selected acid buffers, chelating, non-chelating, and weakly chelating phenols may be differentiated. The action of acetic acid does not depend upon a marked change of pH but is one of simple anion competition; this depends upon the solvent used. A table shows the colour reactions observed with 41 phenols, oximes, and enols in five different solvents, upon the successive addition of pyridine and acetic acid. A prime factor in the stabilisation of the ferric complexes is the ability of a solvent to take up protons from the complexing agent; hence, polar solvents such as water or methanol give the greatest number of chelation results; and non-polar solvents such as benzene, the least. A second table shows the variation of chelation for 27 compounds with six solvents. A test procedure is also described for the demonstration of chelation by pH variation, and the results for 49 compounds are tabulated. There is a discussion of the theory of these chelations in relation to the types of compound, and the constituent groups. J. W. D.

Ultraviolet Analysis of Isomeric Cresol Mixtures. G. P. Carney and J. K. Sanford. Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy: *Anal. Chem.*, **25**, 530 (March 1953).

A simple, rapid method for analysing mixtures of any two or all three isomeric cresols in soln. in *iso*-octane is based on the ultraviolet absorbances of the isomers at 2774, 2728, and 2858 A. The max. error in the determination of each component of synthetic mixtures has been found to be ca. 1·5% (absolute). J. W. D.

Reaction of Sulphonation. XXVI—Estimation of certain Naphthalene-di- and -tri-sulphonic Acids. A. A. Spryskov and B. I. Karavaev. *J. Gen. Chem. U.S.S.R.*, **23**, 254–257 (Feb. 1953).

Exhaustive sulphonation with oleum converts the 1:5-, 1:7-, and 2:6-disulphonic acids of naphthalene into the 1:3:5:7-tetrasulphonic acid, whereas the 1:6 and 2:7 acids are converted into the 1:3:6-trisulphonic acid (the 1:3 acid gives a mixture of tri- and tetra-sulphonic acids). The tetra- and tri-sulphonic acids formed from a mixture of disulphonic acids may be estimated by conversion into acid chlorides with chlorosulphonic acid, the product (isolated by pouring the mixture on ice and filtering) being weighed before and after extraction with benzene, which dissolves only the trisulphonyl chloride. This procedure, in conjunction with the method already devised (see *J.S.D.C.*, **69**, 71 (Feb. 1953)) for analysis of mixtures of the 1:5-, 2:6-, and 2:7-disulphonic acids, enables a full analysis of a mixture of these with the 1:6- and 1:7-isomers to be made. The method is applicable also to mixtures of 1:3:5-, 1:3:6-, and 1:3:7-trisulphonic acids, in which the content of the 1:3:6-acid and the combined content of the other two acids can be determined accurately. A. E. S.

New Oxidation–Reduction Indicators. III—*p*- and *m*-*N*-Phenylaminobenzoic Acids. IV—4′-Sulphodiphenylamine-2-carboxylic Acid. V. M. Cherkasov. *J. Gen. Chem. U.S.S.R.*, **23**, 121–124 (Jan.), 197–199 (Feb. 1953).

In view of the value of *N*-phenylanthranilic acid as an oxidation–reduction indicator—it was first proposed for this use by the author in 1936—examination of the properties of the corresponding *meta* and *para* compounds is of interest, and they are prepared now for the first time, though in low yield, by reaction in presence of copper of *m*- and *p*-iodobenzoic acids with aniline or of iodobenzene with *m*- and *p*-aminobenzoic acids (in previous attempts the chloro compounds have been used). The redox potentials of the three isomers are almost identical, and the *m*- and *p*-isomers, like the *o*-isomer, may be used as indicators in the titration of powerful oxidants.

Reported methods for the preparation of 4′-sulphodiphenylamine-2-carboxylic acid are unsatisfactory. A method for its preparation is described, and its redox properties are examined—they are similar to those of the foregoing compounds. A. E. S.

Identification of Flavonoid Compounds by Filter Paper Chromatography—Additional R_f Values and Colour Tests. H. W. Casteel and S. H. Wender. *Anal. Chem.*, **25**, 508–509 (March 1953).

Tables are given, showing the R_f values of 21 flavonoid compounds, representing 6 different types, for 7 different solvent systems. The colours of 8 of these compounds, both in visible light and in ultraviolet radiation, are also given both for the untreated state and after treatment with each of 7 chromogenic sprays. Joint consideration of R_f values and developed colours often serves to classify a flavonoid compound, especially in differentiating between flavone aglycones and other classes of flavonoid compound, but it is insufficient to differentiate amongst individual flavones with any degree of certainty. J. W. D.

German Standard Specification (DIN 53,802) for the Humidity and Temperature Conditions to be Observed in the Testing of Textiles, the Construction and Conditioning of the Testing Room, the Measurement of the Relative Humidity, and the Conditioning of Test Samples. *Faserforsch. und. Textiltech.*, **4**, 125–129 (March 1953); *Textil-Praxis*, **8**, 337–341 (April 1953).

Characterisation of Warp Streaks in Woven Fabrics — Development and Use of the Streakmeter. H. F. Hume, E. H. Olson, and C. E. Reese. *Text. Research J.*, **23**, 123–129 (Feb. 1953).

The development of an instrument called the *Streakmeter* to locate and characterise individual warp streaks in plain-woven fabrics is described. The instrument measures and records photoelectrically the relative intensities of light reflectances from the yarn and the spaces between the yarns. A. B.

Measurement of Fabric Thickness. R. E. Seaman. *Text. Research J.*, **23**, 262–266 (April 1953).

Various methods for the measurement of fabric thickness are discussed, and it is concluded that the one published by the British Standards Institution involving measurements at low pressures is the most satisfactory. A. B.

Rapid Method for the Estimation of the Readily Accessible Portion of Cellulose. K. Schwabe and H. Frind. *Faserforsch. und Textiltech.*, **4**, 91–99 (March), 174 (correction) (April 1953).

Carbohydrate may be rapidly estimated in cellulose hydrolysates by adding a two- to three-fold excess of standard dichromate to the hydrolysate, warming the mixture, and adding an equal vol. of conc. H_2SO_4; the mixture comes to the boil, and is then allowed to stand for 5 min., when it is diluted with water and titrated with standard ferrous salt (ferroin indicator). This method is used to follow the course of the hydrolysis of cellulose by aq. H_2SO_4, the acid concn., rate of stirring, and liquor ratio being varied. On the basis of the results, a rapid hydrolysis treatment, suitable for the estimation of the readily accessible (amorphous) portion of the cellulose, is developed (90 min., 97°c., liquor ratio 40 : 1, specified conditions of agitation, 3·75 N-H_2SO_4 — the highest concn. for which the swelling effect is substantially the same as that produced by water alone). Hydrolysis–time curves for various cellulose preparations are analysed, and it is found that a first-order equation is obeyed both for reactions proceeding in the amorphous regions and for those occurring in the crystalline regions; the velocity constants are substantially independent of the origin of the preparation. An empirical equation $c = 1{\cdot}28a - a_0$ is derived which enables the fraction of amorphous cellulose (c%) to be determined from one estimation only — the amount hydrolysed after 90 min. (a%); a_0 is a small correction dependent on the type of cellulose preparation. The values obtained for the amorphous fraction are close to those given by other hydrolysis methods and by the periodic acid oxidation and iodine absorption methods. It is considered that the lower values given by these methods, as compared with the values given by X-ray, density, and D_2O-exchange methods, can be explained only in part on the hypothesis that recrystallisation processes occur during hydrolysis. The amorphous fraction is affected only slightly by grinding the preparation; it is not changed when the preparation is dried at 60°c., but is considerably increased when drying is carried out above 100°c.; it is not affected when the cellulose is oxidised (to copper number 8·5) with chromic acid. A. E. S.

Apparatus for Testing Resistance to Abrasion. J. Juilfs. *Wäschereitechn.*, 516 (1952); *Textil-Rund.*, **8**, 145–146 (March 1953).

In Weltzien's apparatus (*Knickscheuerprüfer*), a test piece, 3 cm. wide, is led over two rollers and held by a fixed clamp and another clamp attached to a mobile carriage. The abrasion element oscillates centrally between the rollers. By loading the carriage the tension in the test piece and its pressure against the abrasion element can be varied. A carborundum wedge of defined grain-size serves as abrasion element, but wedges covered with material may be used for special purposes. For assessment, the number of oscillations before break is used. H. E. N.

Colorimetric Test for Assessment of Structural Alteration in the Wool Fibre. M. Robinet and L. Rousseau. *Teintex*, **18**, 155–159 (March 1953).

The Pauly test is used for assessment of alteration in the structure of wool fibres, and is modified by cutting each fibre under test into a series of consecutively numbered fragments, the even fragments being subjected to one treatment and the odd set to another treatment and the two sets being compared. Variations in the wool fibre are shown up. B. K.

Gravimetric Estimation of Proteins precipitated by Trichloroacetic Acid. F. L. Hoch and B. L. Vallee. *Anal. Chem.*, **25**, 317–320 (Feb. 1953).

A study based upon pure human and bovine serum albumin, pure bovine insulin, and crude bovine pituitary extract shows that figures obtained by precipitating them with trichloroacetic acid, and weighing the dried ppt., agree well with figures obtained for cryst. proteins, with protein determinations by measurement of optical density at 280 mμ., and with estimates of weight on a basis of nitrogen determination. Proteins are not hydrolysed, and are quant. removed from soln. A coefficient of variation of ± 3·8% was observed with 5-mg. samples of protein. The influence of mol. wt. on the precipitability of proteins by trichloroacetic acid is discussed; above 12,000, mol. wt. does not appear to be of influence in this respect. A number of applications of the method are indicated, including studies of the hydration of proteins (which become freed from associated org. or inorg. mol.), and the relation of amounts of cations and other mol. dissociated by the precipitating agent from the proteins to their absolute protein dry wt. There are 27 references to the literature. J. W. D.

Modified Photometric Ninhydrin Method for the Analysis of Amino and Imino Acids. W. Troll and R. K. Cannen. *J. Biol. Chem.*, **200**, 803–811 (Feb. 1953).

A modified procedure is described for the photometric determination of amino acids with ninhydrin. Ten of the naturally occurring amino acids give theoretical yields of colour at room temperature. At 100°c. all amino acids, except tryptophan and lysine, react quantitatively. A method for the photometric estimation of hydroxyproline in amino acid mixtures is described. P. G. M.

Determination of the Sequence of Amino Acids in Peptides and Proteins. I — Preparation, Properties, and Chromatographic Adsorption of the Azobenzene-*p*-sulphonyl Derivatives of Various Amino Acids. H. M. Flowers and W. S. Reith. *Biochem. J.*, **53**, 657–662 (March 1953).

A method of preparation of azobenzene-*p*-sulphonyl chloride (sulphazoyl chloride) is described. Some methyl esters of amino acids not previously described in the literature have been prepared by methylation in methanolic hydrogen chloride. *N*-Azobenzene-*p*-sulphonyl derivatives (sulphazoyl derivatives) of various amino acids were prepared by reaction of sulphazoyl chloride with amino acids in aqueous acetone containing $NaHCO_3$. These sulphazoylamino acids were methylated either with methanolic HCl or with diazomethane in dioxan, yielding methyl esters of *N*-sulphazoylamino acids. The chromatographic resolution of mixtures of these methyl esters has been investigated, and the applicability of *N*-sulphazoylation of amino acids to the end-group determination in peptides is discussed. P. G. M.

Two-dimensional Chromatography of Amino Acids on Buffered Papers. A. L. Levy and D. Chung. *Anal. Chem.*, **25**, 396–399 (March 1953).

The secondary resolution of amino acid chromatograms developed with 4 : 1 : 5 butanol–acetic acid–water has previously been most satisfactorily effected using phenol–ammonia; the use of 1 : 1 *m*-cresol–phenol in borate buffer gives, however, superior results. Chromatograms so produced are best run on Whatman No. 52 paper, and they may be completed in 40 hr. The advantages offered by the use of a buffered secondary developer are — (1) The R_f values are more reproducible; (2) the phenol is not discoloured by oxidation; (3) the spots are more compact; (4) the phenol runs more rapidly and with minimal discoloration of the front; and (5) particular separations may be induced by pH control. There are eight pictures of chromatograms in illustration. J. W. D.

Rapid Identification of Fibres by the Christiansen Effect. B. Norwick. *Text. Research J.*, **23**, 259–261 (April 1953).

The measurement of refractive index using the Christiansen effect by immersion of the fibres in liquids of similar refractive indices is described, and a table of synthetic fibres given. A. B.

Identification of Synthetic Fibres by their Refractive Indices and Birefringence. A. N. J. Heyn. *Text. Research J.*, **23**, 246–251 (April 1953).

The central illumination method for the determination of refractive index is described. A method is given for the differentiation of synthetic fibres using refractive indices and birefringence. A. B.

Microscopical Identification of Polyester Fibres (Terylene). W. Bobeth. *Faserforsch. und Textiltech.*, **4**, 45–55 (Feb. 1953).

The behaviour of cut Terylene or other polyethylene terephthalate fibres in phenol (air-moist, melted by slight warming) or in phenol–nitrobenzene (1 : 1) is characteristic of the fibre, but varies in detail according to the setting or other treatment that the fibre has received. The fibre behaves as if it has a resistant skin that is embrittled somewhat by heat-setting treatments, and the first change to be noted is the appearance of a swelling at the fibre end, which may be cup- or mushroom-shaped, the latter being typical of heat-treated fibres. As swelling proceeds, a cylindrical core of unswollen fibre becomes visible, and this terminates in a sharp spike within the swollen end of the fibre. At faulty or damaged places in the fibre, abnormal swelling occurs, and a pair of core spikes may be formed. Dry or wet setting treatments may greatly reduce the rate at which the observed phenomena occur. A. E. S.

Importance of Chromaticity in Evaluation of Whiteness. H. Hemmendinger and J. M. Lambert. *J. Amer. Oil Chem. Soc.*, **30**, 163–168 (April 1953).

The colour of near-white samples of cloth is discussed using the standard C.I.E. system of colour specification. Practical examples of whites and factors influencing whiteness of laundered goods are given. The laboratory evaluation of the colour of materials in detergency tests and laboratory wash tests with chromatic soil have been studied. P. G. M.

Laboratory High-temperature Dyeing Unit. F. F. Jacobs. *Amer. Dyestuff Rep.*, **42**, P 175–P 176 (16 March 1953).

The Ciba high-temperature dyeing unit is described. It consists essentially of a cylindrical autoclave, fitted with two thermometers to record the temp. of steam and of dye liquor. A frame inside the autoclave supports twelve dye-beakers fitted with individual stainless-steel reciprocating agitators driven from an external motor. A. J.

Spectral Energy Distribution of the International Commission on Illumination (C.I.E.) Light Sources A, B, and C. R. Davis, K. S. Gibson, and G. W. Haupt. *Bur. Stand. J. Res.*, **50**, 31–37 (Jan. 1953)—*Research Paper* 2384.

The relative spectral energy distributions of C.I.E. light sources A, B, and C, and the spectral transmittances of filters B and C, are given for the range 320–780 mμ. A. J.

Spectrophotometric Investigation of Reaction of Titanium with Chromotropic Acid. W. W. Brandt and A. E. Preiser. *Anal. Chem.*, **25**, 567–571 (April 1953).

In dil. acid soln. several species of complex coexist, corresponding to different ratios of Ti to chromotropic acid. The whole system is highly sensitive to pH and to reagent concn. in the pH range 4–6, and of the 22 anions and 12 common metal cations studied, several interfere; these include Fe, Mn, Zr, and Cr at concn. of the order of 10^{-5}M. In conc. acid soln. experimental conditions are less critical, and there is less interference from other ions. Experimental procedure and results are given in full, and the latter presented in 8 graphs. Though the same purple colour is formed in both conc. HCl and conc. $HClO_4$ as in conc. H_2SO_4, aq. dilution of the H_2SO_4 soln. results in destruction of the colour, and evidence is presented indicating that this is due to the breakdown of the chromotropic acid–Ti complex by water acting as a reagent, and is not a dilution effect. It is suggested that the method by which this latter aspect is studied may have wider application. J. W. D.

Determination of the Methoxyl Content of Fats. R. R. Allen and R. J. Buswell. *J. Amer. Oil Chem. Soc.*, **30**, 123–124 (March 1953).

A method for the determination of the methoxyl content of fats has been developed using chromotropic acid. The fat is saponified, and the methanol recovered by distillation, oxidised, and treated with chromotropic acid. The optical density of the coloured solution at 5700 A. is proportional to the methoxyl present. P. G. M.

Quantitative Determination of Dithiocarbamates and Thiuram Sulphides. C. L. Hilton and J. E. Newell. Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy: *Anal. Chem.*, **25**, 530 (March 1953).

Zinc dithiocarbamates and thiuram sulphides in rubber are determined by extraction with ethanol, decomposition to yield CS_2, distillation of the CS_2 into an aq. dimethylamine soln., and spectrophotometric analysis of the resulting mixture. Dithiocarbamates are decomposed by heating in ethanol acidified with H_3PO_4, but thiuram sulphides must first be reduced by $NaHSO_3$. Since thiuram sulphides are converted into dithiocarbamates during vulcanisation, the method has been developed in such a way that the dithiocarbamates and thiuram sulphides may be determined separately; the analysis can thus be used to measure the degree of conversion. A sample containing both types of accelerator is extracted and decomposed with acidified alcohol, thus decomposing the dithiocarbamates. The liberated CS_2 is distilled into an excess of dimethylamine (which is optically transparent between 260 and 300 mμ.); the product has absorption maxima at 253 and 287 mμ., and minima at 225 and 270 mμ. Only the absorbance at 287 mμ. is used, as there is interference below 280 mμ. After determination of the dithiocarbamates, the residue is neutralised with dil. NaOH, and an aq. soln. of $NaHSO_3$ is added. The distillation and determination of liberated CS_2 are then repeated. The method shows an accuracy within ± 2% with pure accelerators, and within 1% for accelerators in rubber. J. W. D.

Determination of Formaldehyde in the Presence of Phenols and Phenol Alcohols. J. I. de Jong. *Rec. Trav. chim.*, **72**, 356–357 (April 1953).

The following reactions occur successively—

$$H{\cdot}CHO + CN^- \rightarrow CN{\cdot}CH_2{\cdot}O^-$$

$$CN{\cdot}CH_2{\cdot}O^- + H_2O \rightarrow CN{\cdot}CH_2OH + OH^-$$

and the excess CN^- may be determined by titration with $Hg(NO_3)_2$, diphenylcarbazone being used as indicator (E. Pfeil and G. Schroth, *Z. anal. Chem.*, **34**, 333 (1952)). This procedure may be used to estimate formaldehyde rapidly and accurately, and the reaction is unaffected by phenols, phenol alcohols, or buffers of the acetate or phosphate type; in this it is superior to other methods in common use. Mercuration of any phenols present does not occur, presumably because of the rapidity of the reaction between Hg^{2+} and CN^- ions. The method is described. J. W. D.

Quantitative Determination of Resins—Losses of Resin during Preliminary Treatment of Samples. S. Kündig. *Textil-Rund.*, **8**, 153–156 (April 1953).

In stripping a dye with sodium hydrosulphite, 10–70% of melamine–formaldehyde resin (I) is removed also. Urea–formaldehyde resin (II) is lost even more readily. If starch has been fixed with I, the only adequate method of analysis is to extract all the finish with water (pH 6·6–7·0) at 75° C., and to determine H·CHO and nitrogen. Less than 1% of I is lost by treatment with ether, alcohol, water, or pancreatic enzyme, but under similar conditions 20–55% of II is removed. In the latter case, it is shown that the higher the temp. of hardening, the less II is lost in the treatments. H. E. N.

Rapid Determination of Mineral Components in Pulp. E. Moosmüller. *Papier*, **6**, 523–524 (1952); *Chem. Abs.*, **47**, 4605 (10 May 1953).

The pulp (5–20 g.) is treated with 35% H_2O_2, warmed to 40–50°C., and treated with conc. H_2SO_4 added in drops at such a rate that the localised brown coloration is rapidly destroyed by the H_2O_2; large excess of H_2O_2 must be avoided. Ordinarily the organic matter will be completely converted into CO_2 in 5–10 min. The mixture is

then heated until strong fumes of SO_3 are evolved. Darkening of the mixture is prevented by adding 1–2 drops of H_2O_2. The cooled mixture is treated with 50 c.c. aq. HCl, and SiO_2 determined in the usual way. Metals are determined in the filtrate. The results compare well with those obtained by methods taking much longer; the SiO_2 yields are usually slightly higher by this method.
C. O. C.

Gloss of Papers. V. G. W. Harrison and S. R. C. Poulter. *Nature*, **171**, 651 (11 April 1953).

A psychophysical study of the gloss of several series of coated and uncoated papers differing widely in surface finish and in colour shows that considerable disagreement is found among the judgments of individual observers, and marked shifts in ranking occur when conditions of illuminating and viewing the specimens are changed. The equation—

$$\text{Gloss} = S(0{\cdot}390 + 0{\cdot}325 \tanh 20/L) - 100 \tanh [0{\cdot}115\,S\,(P - 1)/100]^2$$

(papers are illuminated by a nearly parallel beam incident at 45°; S = intensity of light reflected at the specular angle (45°); L = intensity in the direction of the normal (0°); and P = ratio of intensity at 45° to that at 40°) is considered to be suitable as the basis of a practical method of gloss specification.
J. W. B.

Wet Rub Tester for Mineral-coated Surfaces. B. W. Attwood. *Proc. Tech. Sectn. British Paper & Board Makers' Assocn.*, **33**, 667–681 (Dec. 1952).

The nature of the wet rub test as applied to mineral-coated paper and boxboard, and methods used in carrying out the test, are briefly described. A new apparatus, which is objective and gives consistent results in close correlation with the finger test, consists of a constant-speed (53·8 r.p.m.) turntable carrying a clamp to take an aluminium dish in which the test sample is secured. A pad of standard pencil-eraser rubber, attached to an arm, rests on the test sheet at a fixed and controllable pressure. In developing a standard testing procedure, the effect of the time of contact and the weighting of the rubber pad, the temperature of the water, and the time of soaking were investigated as well as the conditioning of the surface of the rubber pad. The tester was applied to show the enormous hardening effect of formaldehyde on the coating, and the hardening effect of maturing the samples. In its final form the test comprised grinding the rubber pad (2 cm. × 2 cm.) dry for 5 min. with Durex J 320 carborundum cloth, under a weighting of 250 g.; washing out the dish and cleaning the pad; mounting the sample, adding 40 ml. of water at 65–70° F., and switching on the motor; after a few seconds applying the pad and leaving in contact for 30 sec.; and switching off the motor, collecting the aqueous suspension of coating, and matching with standard dilute coating slips.
S. V. S.

Analysis of Phthalic Esters of Cellulose and of Polyvinyl Alcohol. C. J. Malm, L. B. Genung, and W. Kuchmy. *Anal. Chem.*, **25**, 245–249 (Feb. 1953).

Phthaloyl content can be measured by titration with 0·1 N. alkali, or by ultraviolet absorption at 275 mμ. Some of the usual methods for determining saponification value (Eberstadt, or soln. method), ethoxyl, and hydroxyl (acetylation) are directly applicable to mixed esters and ether–esters such as cellulose acetate phthalate and ethyl cellulose phthalate. Free phthalic acid, if present, may often be removed either by ether extraction or by a reprecipitation method, and then titrated. Several combinations of data allow the calculation of the free acid without direct estimation. Equations and nomographs are given for the conversion of percentage results into degrees of substitution. Numerous data of actual analyses are given, illustrating the validity of the methods, all of which are described in detail. There are 32 references to the literature.
J. W. D.

Overall Basicity of Chrome-tanned Leather. R. L. Stubbings and E. R. Theis. *J. Amer. Leather Chem. Assocn.*, **48**, 155–168 (March 1953).

A method, based on the rapid complexing activity of oxalic acid, is described for the determination of the overall basicity of both chrome liquors and chrome-tanned leathers. The technique is not complicated, and can be applied to liquor or leather containing Fe or Al salts.
J. W. B.

Polarographic Determination of Phthalate Esters in Plastics. G. C. Whitnack and E. St. C. Gantz. *Anal. Chem.*, **25**, 553–556 (April 1953).

A rapid and convenient method is detailed whereby phthalate esters used as plasticisers, e.g. in plastic coatings, may be determined by the polarographic analysis of soln. of polymer and plasticiser in a suitable solvent such as acetone or ethanol, in presence of tetramethylammonium chloride as supporting electrolyte (suitable for use at high negative potentials). A standard graph of wave-height *versus* concn. is prepared, and used as reference in subsequent analyses. The precision of the method is ~ 15 parts per 1000. Data are given (diffusion currents, diffusion current constants, and half-wave potentials) for dimethyl, diethyl, dibutyl, dioctyl, and diphenyl phthalates.
J. W. D.

PATENTS

Apparatus for Measuring Yarn or Filament Diameter. T. M. M. (Research). *BP* 691,491

Apparatus for measuring the diameter or variations in diameter of a yarn, filament, etc. comprises a barrier-layer photoelectric cell and a light source, means for traversing the filament between them, and a sensitive instrument for measuring, without an intervening amplifier, the current output from the cell. The instrument actuates a servo-mechanism, which in turn operates a stylus which coacts with a moving chart.
J. W. B.

Determining the Moisture Content of Stationary or Moving Goods. K. Trischberger. *BP* 691,332

In apparatus of the type in which air is drawn from near the goods and through a hygrometric electrode assembly whose electric properties vary according to the moisture content of the air passing through it, the electrode assembly comprises spaced metallic conductors mounted in or on a layer of fabric made from natural or artificial fibres, the conductors forming part of a circuit whose resistance varies according to the moisture content of the ambient atmosphere. Use of nylon fabric has the advantage that it does not absorb moisture.
C. O. C.

Apparatus for Performing Calculations relative to Colour Matching. American Cyanamid Co. *BP* 691,671

There are two characteristics of pigment reflection each of which is independently additive. One factor is the specific light absorption, which is the same as the function K for a dye—

$$CK = \frac{(1 - b)^2}{2b}$$

(b = body reflection, C = dye concentration). The other (S) is an analogous function for the light-scattering effect of pigment particles which, while not the same as K, and changing in a manner quite different from K, is nevertheless additive. Both these functions remain additive when multiplied by concentration. The total light reflectance is proportional not to the sum of the values of CK or CS but to the ratio of the sums of the values of CK to those of CS. Apparatus is described which enables additive physical quantities to be produced proportional to these sums.
C. O. C.

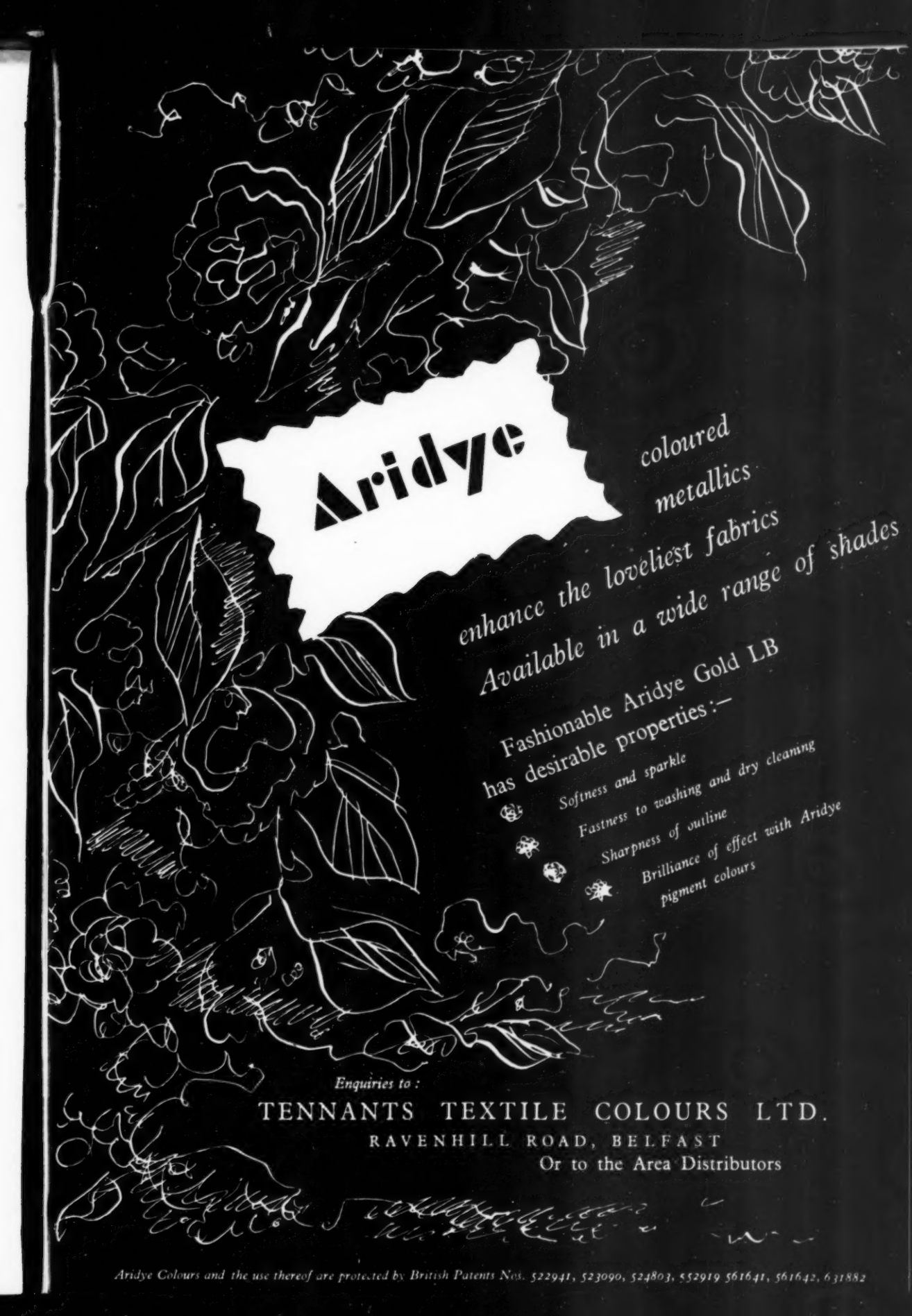
Relationship between Various Surface Properties of Wool Fibres. I—Methods for Estimating Wool Fibre Modification (VI p. 308).
Relationship between Various Surface Properties of Wool Fibres. II—Frictional Properties (VI p. 308).
Infrared Spectra of Model Amides, Polypeptides, and Proteins (VI p. 308).
Birefringence of Dacron Polyester Fibre (VI p. 309).
Effect of Heat and Light on Polyvinyl Chloride (XIII p. 312).

XV— MISCELLANEOUS

Uptake of Dyes into Cut Leaves. A. Charles. *Nature*, **171**, 435–436 (7 March 1953).

Dermatitis from Hexamethylenediamine. G. Doverneuil and G. Buisson. *Arch. Maladies profess. Méd. Travail et Sécurité sociale*, **13**, 389–390 (1952): *Chem. Abs.*, **47**, 3571 (10 April 1953).

Dermatitis caused by hexamethylenediamine affected four workers in a nylon factory. It yielded readily to therapy, but reappeared rapidly if work was resumed.
C. O. C.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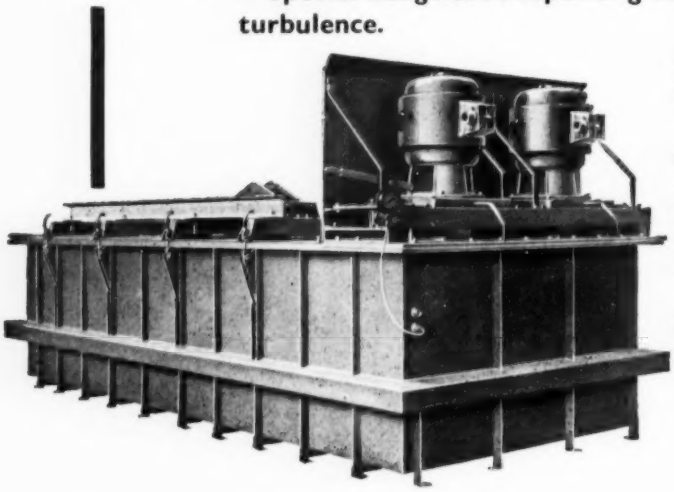

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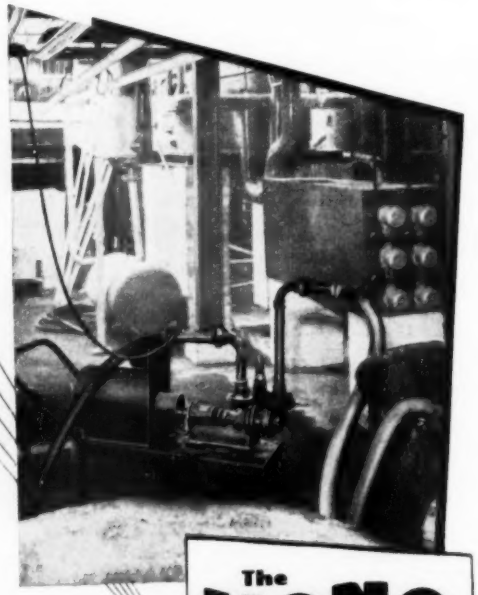

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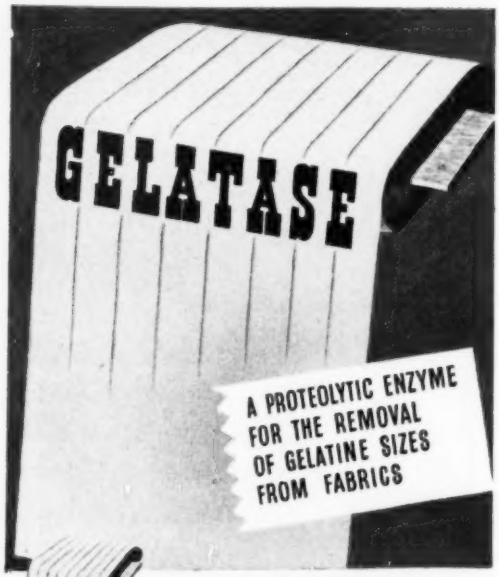

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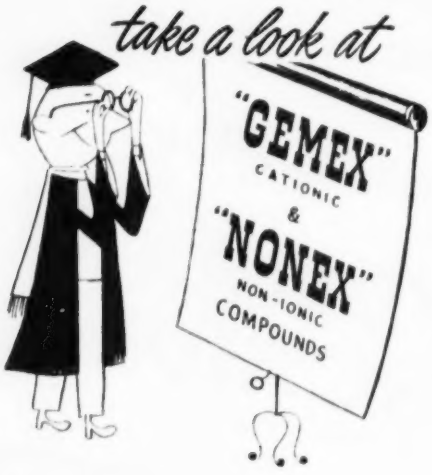

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THIS

...OR THIS?

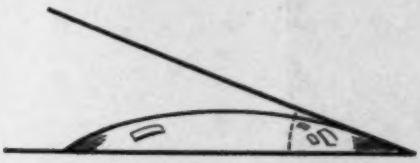

Illustration of negative wetting (angle of contact greater than 90°) and positive wetting (angle of contact 90° or less)

Refer to us if WETTING is a problem in your production

We market what we believe to be the most powerful Wetting Agent available today, and feel that it may be of great assistance in your wetting and dispersing problems. *Literature and samples on request.*

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